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Studies in Molecular Luminescence.

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by

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ABSTRACT

This Dissertation is mainly concerned with the transfer of triplet state energy by radiationless processes. These processes are studied by means of their effects on observable radiative events.

Two main approaches are taken in these studies:

1) phosphorescence and fluorescence excitation spectra are employed to determine if there is quenching or intersystem crossing at energy levels which are higher than the ground vibrational levels of the S_1 and/or T_1 excited states of molecules;
2) luminescing solutes in solid matrices are studied by means of the temperature dependence of the phosphorescence lifetime; this approach is used in three different types of system:
   a) aromatic solutes in crystalline aromatic solvents;
   b) aromatic solutes in polymethylmethacrylate (lucite);
   c) aromatic solutes in alcohols.

The first of the two approaches, the study of excitation spectra, yielded only moderately good results. It appears that there is considerable quenching at levels of higher energy than the ground vibrational levels of excited states.

The second of the two approaches yielded good results in the case of the mixed crystal systems. It has been shown, quite conclusively, that the main radiationless transfer of triplet state energy is intermolecular, not intramolecular.

Our approach with aromatic solutes in plastics was proper: thereis, as in the case of mixed crystals, thermal transfer of triplet state energy. This was not demonstrated by us, however, but by others.

The study of aromatic solutes in alcoholic solvents, the last type of system discussed, merely provides a collection of strange data about the temperature dependence of phosphorescence.

GENERAL INTRODUCTION

Molecular luminescence enables the investigator to study not only the electronic structure of certain molecules but also intermolecular interactions evidenced in solvent effects, in molecular complexes, in pure and mixed crystal systems, in external heavy-atom spin-orbit coupling effects - to name but a few.

The phenomenon of molecular luminescence is a directly observable event which, because of the various qualitative and quantitative changes to which it is subject, facilitates the study of processes which are not themselves directly observable. A class of processes which is of this type and which is also of central importance to the disposition of energy among excited electronic levels is radiationless transitions. Three important theoretical papers[1-3] concerned with non-radiative transitions have appeared recently; these have stimulated considerable interest in experimental studies which promise to provide a better understanding of this type of depletive event. This Dissertation is, at least partially, an outgrowth of this interest. It is thought that the work reported here will increase considerably our store of knowledge concerning non-radiative quenching events.

The work reported here is concerned almost exclusively with the temperature dependence of phosphorescence intensity and lifetime. The specific object of this work is to provide some understanding of these non-radiative events which connect the lowest triplet state to the ground singlet state; other depletive events, however, will be touched on from time to time.

CHAPTER I

FLUORESCENCE AND PHOSPHORESCENCE EXCITATION SPECTRA

1. Introduction

a) General

An excitation spectrum is a spectrum which is made in the following manner: the intensity of fluorescence (or of phosphorescence) from an aggregate of luminescing molecules, all of one kind, is plotted *versus* the wave-length (or wave-number or reciprocal wave-length) of a constant intensity excitation radiation. The spectrum which is made by this method can shed some light on questions about certain processes which are thought to occur intramolecularly and radiationlessly.

Fluorescence and phosphorescence quantum yields have been studied by Parker and coworkers[4-8] and by Weber and Teale[9,10]. This work has led Parker *et al.* to make excitation spectra of both types of luminescence in order to compare their relative quantum efficiencies at different excitation wave-lengths.

b) Theory

Molecules which are capable of luminescing are readily subjected to studies which employ excitation spectra. Figure 1 illustrates, in terms of a Jablonski diagram, a molecule which can both fluoresce and phosphoresce. Figure 2 is a potential energy diagram showing the higher vibrational levels from which intersystem crossing and singlet and triplet quenching may be supposed to occur. The molecule is excited by means of I_0 to the vibrational levels of the first excited singlet state; this energy may be vibrationally degraded to the lowest vibrational level of the first excited singlet state from where it may

FIGURE 1. Jablonski diagram of a simple system consisting of a singlet ground state, S_0, of a first excited singlet state, S_1, and a lowest triplet state, T_1. The arrows represent transition processes and the k's - or in one instance: $k_Q[Q]$ - represent the first order rate constants for those processes.

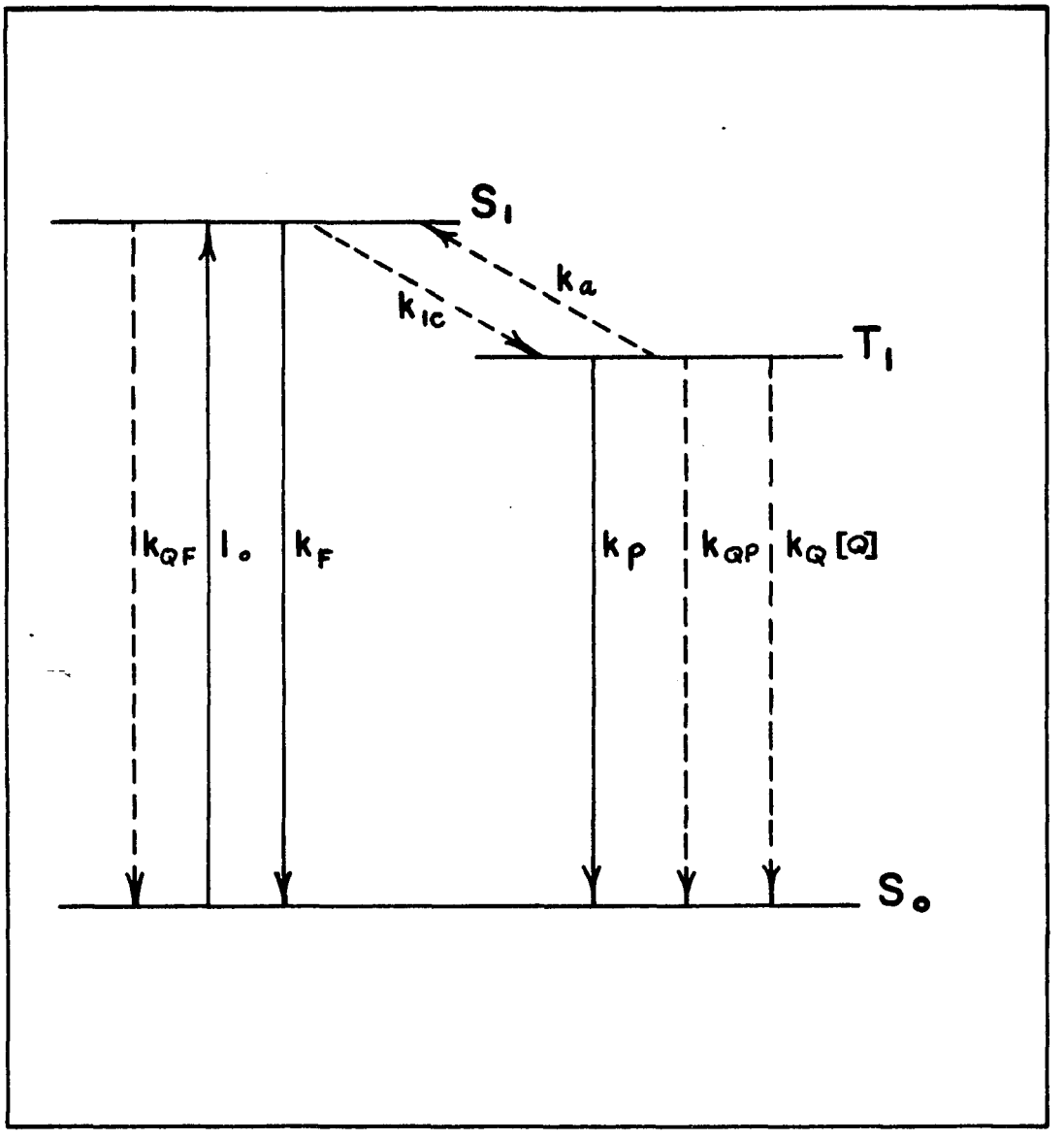
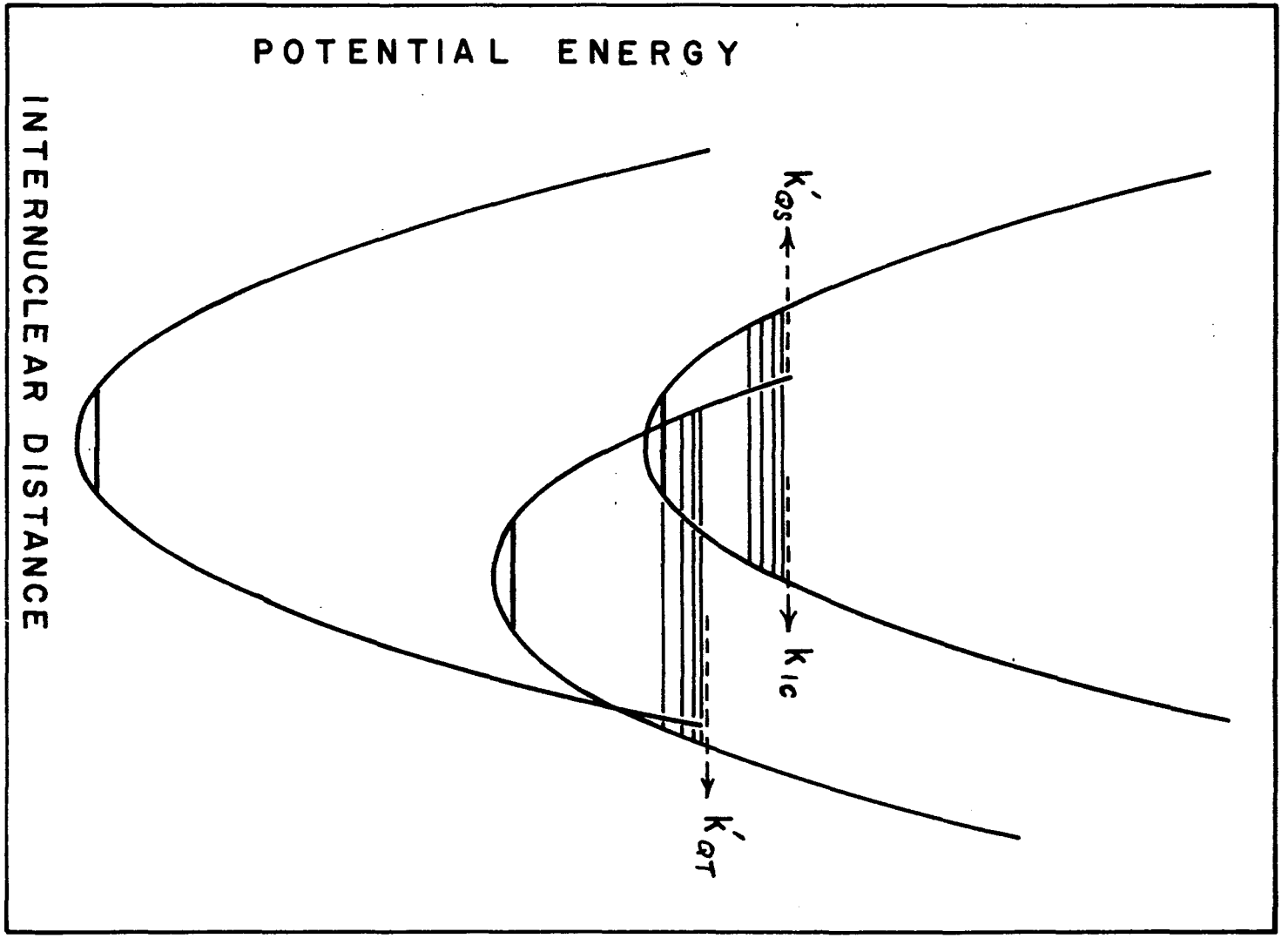

S1
ka
kIC
T1
kQF
I0
kF
kP
kQP
kQ [Q]
S0

FIGURE 2. Potential energy curves for a system which may undergo quenching in higher vibrational levels of either the first excited singlet or the lowest energy triplet state. The symbol k_{IC} represents the rate constant for intersystem crossing.


POTENTIAL ENERGY
INTERNUCLEAR DISTANCE
K'_{QS}
K_{IC}
K'_{QT}

fluoresce with rate constant k_F. However, this energy may also be converted to heat by an internal conversion process; the rate constant for this process is denoted k_{QF}. A third possibility is that this energy may pass over to the lowest triplet state; this intersystem crossing rate constant is denoted k_{IC}. These are the only postulated depletive processes for energy in the first excited singlet state of "well-behaved" molecules. That portion of the energy which achieves the triplet state is subject to four depletive processes:

1) The molecule may phosphoresce; the rate constant for this process is k_P.

2) The triplet state energy may be internally quenched; the rate constant for this process is given by k_{QP}.

3) The triplet energy may also be externally quenched. The extent of such an impurity quenching is proportional to the concentration of the impurity; this process possesses a first order rate constant $k_Q[Q]$, where [Q] denotes the concentration of the impurity.

4) Energy may be thermally activated through successively higher vibrational levels of the T_1 state until quasi-degeneracy with the zero-point level of the S_1 state obtains. Energy transfer then occurs to the S_1 state, whence it may undergo internal conversion, fluorescence, etc., as previously specified. The rate constant for this thermally activated event is denoted k_a.

The efficiencies of phosphorescence and fluorescence are expressed as a quotient of rate constants. The efficiency of fluorescence is represented by θ_F where

$$\theta_F = \frac{k_F \Phi_S}{k_F + k_{QF} + k_{IC}} . \qquad (1)$$

The symbol Φ_S represents the efficiency of singlet formation; it is a function of the wave-length of I_O, the exciting light intensity, and of k_a, the rate constant for triplet state thermal activation. All these processes are tabulated in Table I. The phosphorescence efficiency, θ_P, is likewise a quotient of such terms:

$$\theta_P = \frac{k_P \Phi_T}{k_P + k_{QP} + k_Q[Q] + k_a} . \qquad (2)$$

Here, Φ_T deontes the efficiency of triplet state formation.

Provided that all depletive processes have been accounted for, these two luminescence efficiencies, θ_F and θ_P, are constant quantities when Φ_S and Φ_T, respectively, are constant. It follows immediately that if light energy is absorbed by an aggregate of luminescing molecules, the fraction of this energy that is transformed into luminescence will be a fixed quantity, provided the excitation wave-length is not changed. It is recognized, however, that θ_F and θ_P do vary with excitation wave-length, for the absorption spectrum certainly influences Φ_S and, of course, Φ_T. The luminescence efficiencies, θ_F and θ_P, are not wave-length dependent other than through the absorption spectrum, if the various rate constants are independent of wave-length. The suggestion then asserts itself that phosphorescence and fluorescence may, under certain conditions, be separately monitored to record their intensities as a function of the wave-length of the exciting light. Provided the conditions mentioned above are attainable then both excitation spectra should be identical and they should replicate the absorption spectrum if we possess ideality (or correct for non-ideality) of photomultiplier tube response and instrument geometry.

TABLE I

PROCESS		RATE CONSTANT
$S_0 \longrightarrow S_1$	Excitation	
$S_1 \longrightarrow S_0$	Fluorescence	k_F
$S_1 - - - - - - \rightarrow S_0$	Fluorescence quenching	k_{QF}
$S_1 - - - - - - - \rightarrow T_1$	Intersystem crossing	k_{IC}
$T_1 - - - - - - \rightarrow S_1$	Thermal activation to singlet manifold from triplet manifold	k_a
$T_1 \longrightarrow S_0$	Phosphorescence	k_P
$T_1 - - - - - - - \rightarrow S_0$	Phosphorescence quenching	k_{QP}
$T_1 \xrightarrow{[Q]} S_0$	Impurity quenching	$k_Q[Q]$

It is well-known that photomultiplier response is wave-length dependent. If the wave-length response curve is known this dependence may be corrected for; influences of instrument geometry can be treated similarly. Another consideration is the spectrum of the exciting light source, the output of which must also be known. This output is contained in the factor θ_F. Consequently, this factor must be corrected so that θ_F becomes dependent only on the absorption spectrum.

The dependence of θ_F on the absorption spectrum may be shown in the following manner. The fluorescence intensity if proportional to the amount of light absorbed by the aggregate of luminescing molecules; this is given by the equation

$$I_F = k(I_o^\lambda - I^\lambda) \quad . \tag{3}$$

Factoring out I_o^λ, we get

$$I_F = kI_o^\lambda \left(1 - \frac{I^\lambda}{I_o^\lambda}\right) \quad . \tag{4}$$

However, I/I_o is the transmittance and is expressed by the equation

$$\frac{I^\lambda}{I_o^\lambda} = 10^{-\epsilon_\lambda c} \quad . \tag{5}$$

for an absorption pathlength of 1 cm. Equation (5) expresses transmittance in terms of the molar decadic extinction coefficient of the absorbing species, ϵ_λ, and the concentration of the absorbing-luminescing solute, c. This may be expressed differently by substituting (5) into (4) with the following result:

$$I_F = kI_o^\lambda (1 - 10^{-\epsilon_\lambda c}). \tag{6}$$

For small $\epsilon_\lambda c$, the following approximation may be made:

$$1 - 10^{-\epsilon_\lambda c} \cong 2.303\ \epsilon_\lambda c \tag{7}$$

Substituting (7) into (6) gives

$$I_F = k' I_o^{\lambda} \epsilon_{\lambda} c \ . \qquad (8)$$

This equation states that the intensity of fluorescence from an aggregate of molecules will be proportional to the molar extinction coefficient if the concentration is held small and constant, and if I_o^{λ} and k are constant for all λ. A similar development may be made for phosphorescence intensity. The value of k in this latter instance will be different from the former; the equation may be expressed as follows:

$$I_P = k'' \ I_o^{\lambda} \epsilon_{\lambda} c. \qquad (9)$$

c) Limitations of the theory

The considerations above are valid for "well-behaved" luminescing molecules. By "well-behaved" one means that only the processes which are postulated in Table I occur. Perhaps other processes, not stated in Table 1, occur. An example of such a process is the quenching of singlet state energy from higher energy vibrational levels of the S_1 state. Processes of intersystem crossing from higher energy vibrational levels of S_1 are also feasible. These additional processes are shown by arrows in Figure 2. The rate constants are also given for these processes in Figure 2. Should, for some particular wave-length, a constant such as k'_{QS} (i.e., the constant for singlet state quenching at a higher vibrational level) become operative this would alter the value of θ_F; k'_{QS} would have to be added to the denominator of equation (1). Equation (2) would similarly be altered by k'_{QT}, the constant for triplet state quenching at some higher vibrational level of T_1. If such processes be operative, the excitation

spectrum, whether of phosphorescence or fluorescence, will not replicate each other or the absorption spectrum. Parker and Hatchard[4] report that such behavior has been seen by Bauer and Baczynski when studying fluorescein in boric acid glass. Parker and Hatchard[6] also claim to observe such behavior in eosin solutions.

d) Statement of the problem

If one wishes to study radiationless processes of luminescing solutes in complex systems such as mixed crystals, it is desirable to see if the solute exhibits intersystem crossing and/or quenching in higher energy vibrational levels. If it does not, the luminescing compound should yield an excitation spectrum which replicates the absorption spectrum.

Three compounds, chrysene, benzophenone and hexahelicene, were studied by means of excitation spectra. Chrysene was used in mixed crystal studies; it is of importance to know if this compound could undergo depletive processes in higher vibrational levels of the lowest excited singlet and/or triplet levels. Hexahelicene is a unique compound which exhibits D and L forms because of its helical structure; it is an aromatic. Benzophenone was first studied to see if sufficient sensitivity could be attained with the available equipment, as well as to see if higher energy quenching processes occur in this molecule.

2. Experimental

a) Apparatus

The apparatus employed in these studies was an Aminco-Keirs Spectrophosphorimeter. The samples were put into quartz tubes for study. The tubes had an inside diameter of 2mm. where the exciting

light impinged. Liquid nitrogen was used to solidify the samples to a glass. A quartz dewar contained the liquid nitrogen which kept the temperature of the sample at 77° K while measurements were made. Quartz tubes and dewars were obtained from the American Instrument Company. This quartz apparatus did not luminesce.

b) Chemicals

Chrysene was obtained from B. N. Srinivasan who had purified it for mixed crystal work. Hexahelicene was obtained from Professor M. Newman of The Ohio State University; it was used as obtained. Benzophenone was obtained very pure by the employment of preparative gas chromatographic techniques.

The solvents were purchased from the Hartmann-Leddon Company. They were tested for luminescence before use in this work. If fluorescing or phosphorescing impurities were found to be present, the solvent was rejected.

c) Preparation of solutions

The approximation of equation (7), namely

$$1 - 10^{-\varepsilon c} \cong 2.303\ \varepsilon_\lambda c \qquad (7)$$

is valid only when $\varepsilon_\lambda c$ approaches zero; therefore, as an approximation, εc may be as large as 0.02. This means that the product of the molar extinction coefficient, ε_λ, and the concentration, c, should not exceed 0.02. This results in a solution which has a transmittance equal to 0.95. Solutions with this transmittance were prepared in order to make fluorescence excitation spectra. The self-absorption of the fluorescence emission by solutes is also a reason why solutions must be kept dilute.

Phosphorescence presents no problem with self-absorption but the approximation of equation (7) is valid only for low concentrations; therefore, the solution strength should be such that the transmittance again does not fall below 0.95 so that equation (7) is valid.

d) Correction factors for excitation spectra

1) Light source. Light source intensity changes with wave-length; therefore, a correction factor curve must be made for this variable. A standard photomultiplier tube of known response curve is used. Between the photomultiplier tube and the excitation monochromator is a slit arrangement to reduce the amount of light impinging on the photomultiplier tube. A spectrum is made of the light source on a recorder. Two variables must be corrected for:

i) The photomultiplier tube response; this correction factor curve is given in Figure 3.

ii) The intensity variation of the source with the wave-length.

The following expression is given for making these correction factors at a given wave-length, λ:

$$R_\lambda I_\lambda f_\lambda = c, \tag{10}$$

where R_λ is the photomultiplier tube response for that wave-length taken from the response curve and I_λ is read from the spectrum of the light source made as described above. The symbol, f_λ, is the correction factor at wave-length λ. The factor, c, is an arbitrary number which is chosen to facilitate the plotting of the correction curve. The wave-length range of the absorption spectra of interest here is covered by these correction factors. The I_λ correction factor curve is shown by Figure 4.

FIGURE 3. Photomultiplier tube correction factor curve for RCA 1P28.

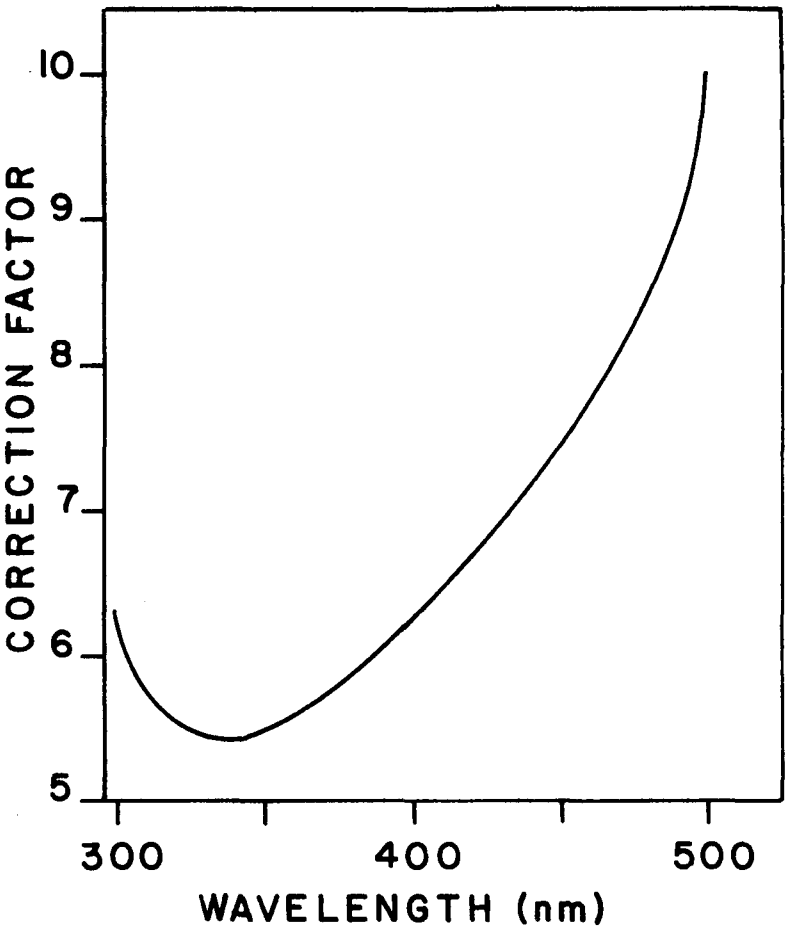
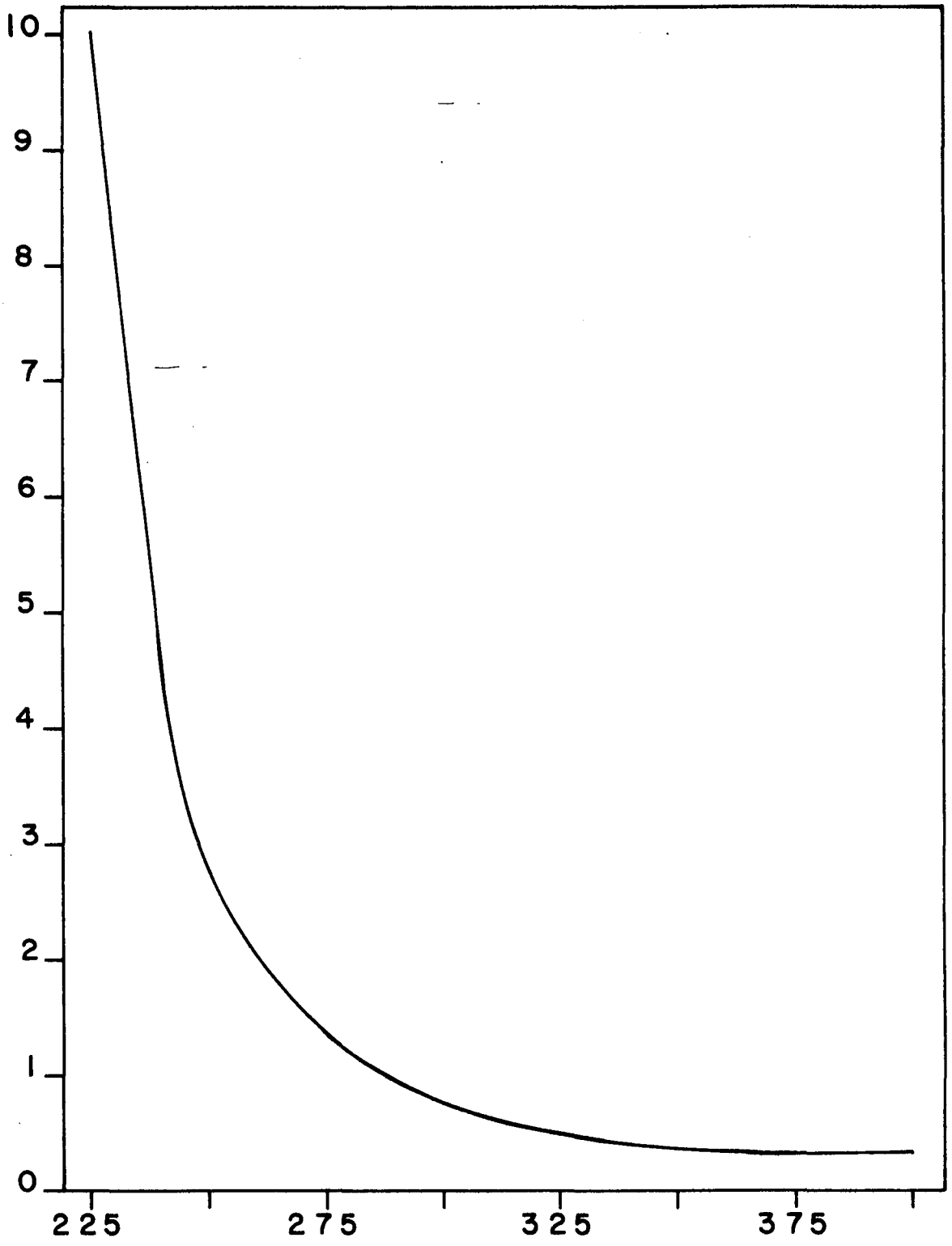

10
9
8
7
6
5
CORRECTION FACTOR
300
400
500
WAVELENGTH (nm)

FIGURE 4. Light source intensity correction factor curve for 500 Va Xenon lamp.


10
9
8
7
6
5
4
3
2
1
0
225
275
325
375

2) Slits. Slits must sometimes be changed during the course of making excitation spectra; consequently, corrections for such a change must be made. The determination of this factor is done after the excitation spectrum has been made and when it is known which slits had been altered. A detergent solution is put into the sample compartment and the intensity of the scattered light is measured with some one of the slit arrangements used in making the excitation spectrum. The intensity is recorded and the slit arrangement is varied in the same way as it was altered when making the excitation spectrum. The intensity at any one of the specific arrangements may be chosen as the standard to which all others are to be referred; the correction factor is then easily determined as follows:

$$\frac{I_{s_1}}{I_{s_2}} = f_s \ , \qquad (11)$$

where I_{s_1} is the intensity through the slit arrangement taken as a standard, and I_{s_2} is the intensity through a different slit arrangement and is the intensity to be standardized by the slit correction factor f_s.

3) Electronic amplification. On the Aminco-Keirs Spectrophosphorimeter are two devices for amplifying the signal, the meter multiplier, and the sensitivity control. When making excitation spectra it is often necessary to change these by large increments. The meter multiplier correction factor may be read directly off the instrument. The sensitivity control, however, must be calibrated; the setting on the knob goes from 0 to 15 as the signal amplification goes from 1 to 3.5. Correction factors are made for this variable as in equation (10) where the curve of amplification-of-signal versus knob-setting is

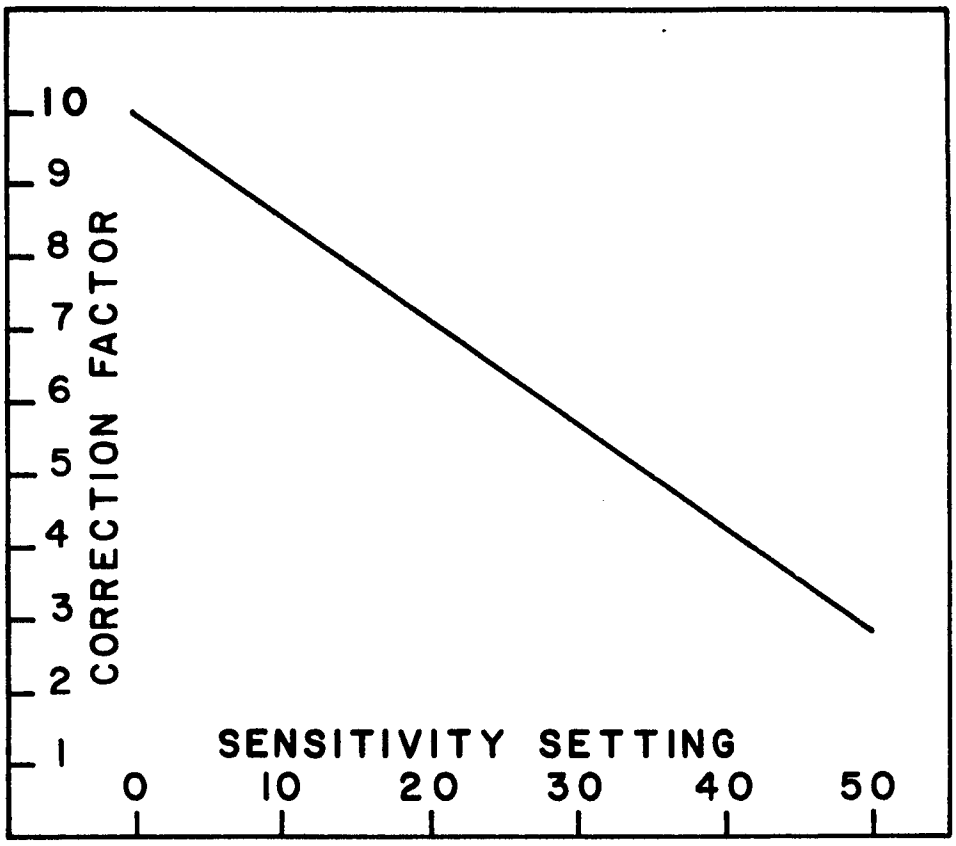
obtained. This is also obtained by amplifying the scattered light intensity signal from a detergent solution and recording the intensity for each knob setting. The correction curve is made as described above; the calibration curve is shown in Figure 5.

e) Obtaining an excitation spectrum and how to correct it

As stated above, an excitation spectrum is obtained by monitoring phosphorescence or fluorescence and recording its intensity as a function of the wave-length of the exciting light. Care must be exercised to prevent scattering of the exciting light onto the phototube. This difficulty is encountered when monitoring fluorescence since the rotating phosphorescope "can" cannot be used. Small slits on the excitation monochromator side of the sample aid in reducing this problem; small slits here, however, are also necessary in order to obtain good excitation spectrum resolution. The slits on the emission monochromator side of the sample are opened as wide as possible to collect all the available light; this enables the experimenter to keep electronic amplification and, consequently, the signal-to-noise ratio at a lower level.

The spectrum which is desired may have to be made in several steps. As was seen earlier, the product ϵc should equal ~ 0.02. The value of ϵ may vary by nearly four orders of magnitude throughout the absorption spectrum, necessitating the preparation of a solution of different concentration for each transition envelope. Thus, another correction factor must be applied to each excitation spectrum so as to standardize on a single solute concentration. It is usual to overlap wave-length regions with information about the corresponding emission intensities. When a given wave-length region is covered with two

FIGURE 5. Sensitivity control correction factor curve. American Instrument Company Spectrophosphorimeter.


10
9
8
7
6
5
4
3
2
1
CORRECTION FACTOR
SENSITIVITY SETTING
0
10
20
30
40
50

excitation spectra resulting from changes in concentration, the lower concentration spectrum should be used as long as intensity can be read to two significant figures.

Concentration, sensitivity, slit width, and meter multiplier correction factors should be tabulated as corrections for the emission spectrum chosen. The wave-lengths which are tabulated dictate which values of Figure 4, the light source intensity correction curve, are to be used. The values from Figure 4 are tabulated for that wave-length. The correction factors of Figure 3 are to be used only if the wave-length setting of the emission monochromator is changed. The elements of the rows (across) are multiplied together; this product is the corrected values of intensity. When these products are plotted against wave-length, the result is an excitation spectrum. Molecules which show no quenching nor intersystem crossing at higher vibrational levels of excited states should have excitation spectra which replicate their absorption spectra.

3. Results and Discussion

a) Benzophenone

Benzophenone was studied by making excitation spectra using 3-methylpentane as the solvent. The correction factors were applied as discussed in the experimental section. The phosphorescence peak at 442 mμ (Figure 6) was monitored. Small (0.5 mm) slits were used in the excitation monochromator to improve the resolution of the excitation spectrum. Large emission slits were used to gather as much light as possible from the sample.

The final corrected curve is shown in Figure 7. Comparison of Figure 7 with Figure 8, a room temperature absorption spectrum in

FIGURE 6. Benzophenone in 70% ethyl alcohol, 30% isoamyl alcohol; low resolution for phosphorescence emission (right), good resolution for excitation spectrum (left).

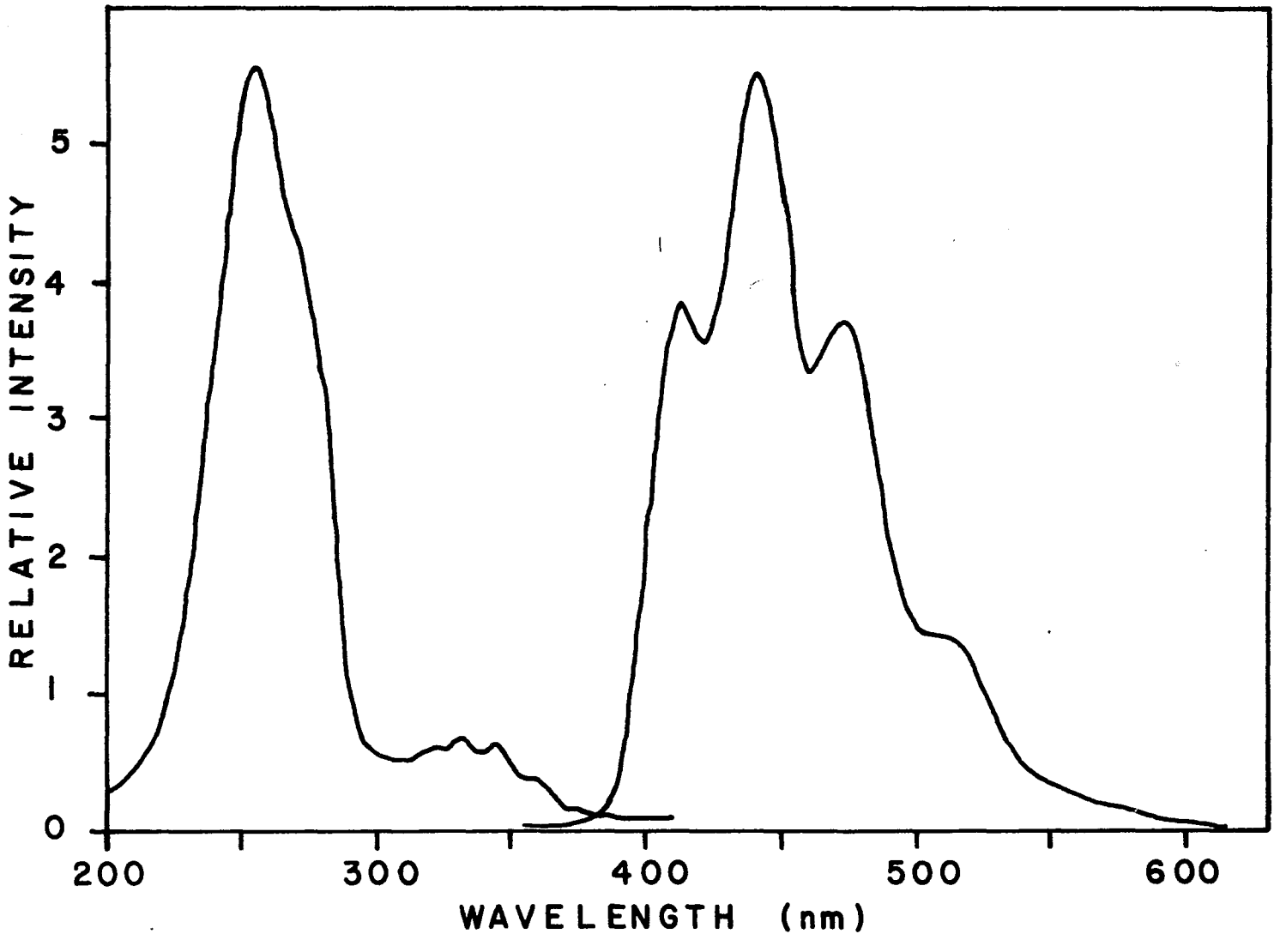

RELATIVE INTENSITY
0
1
2
3
4
5
200
300
400
500
600
WAVELENGTH (nm)

FIGURE 7. Corrected excitation spectrum of benzophenone in 3-methylpentane.

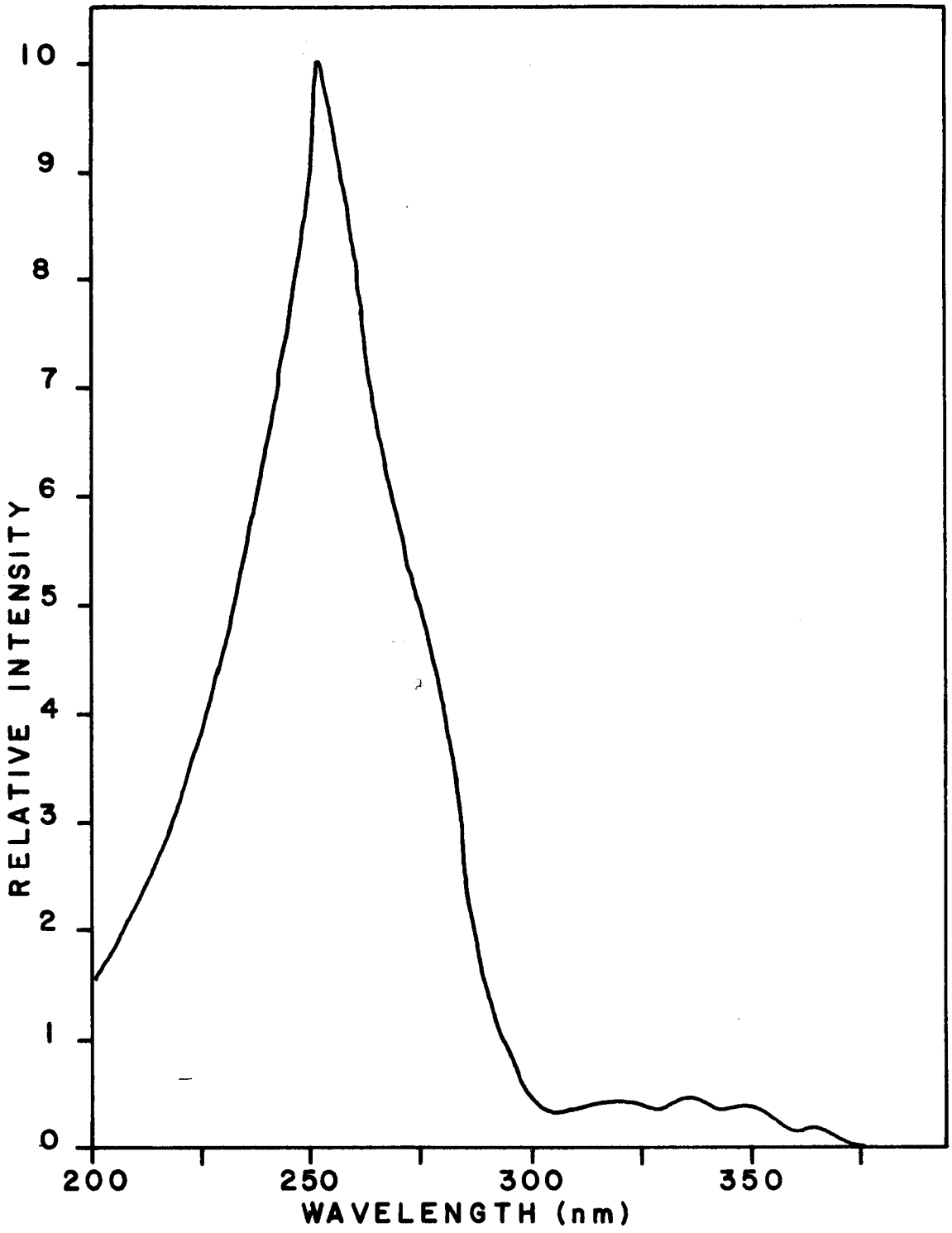
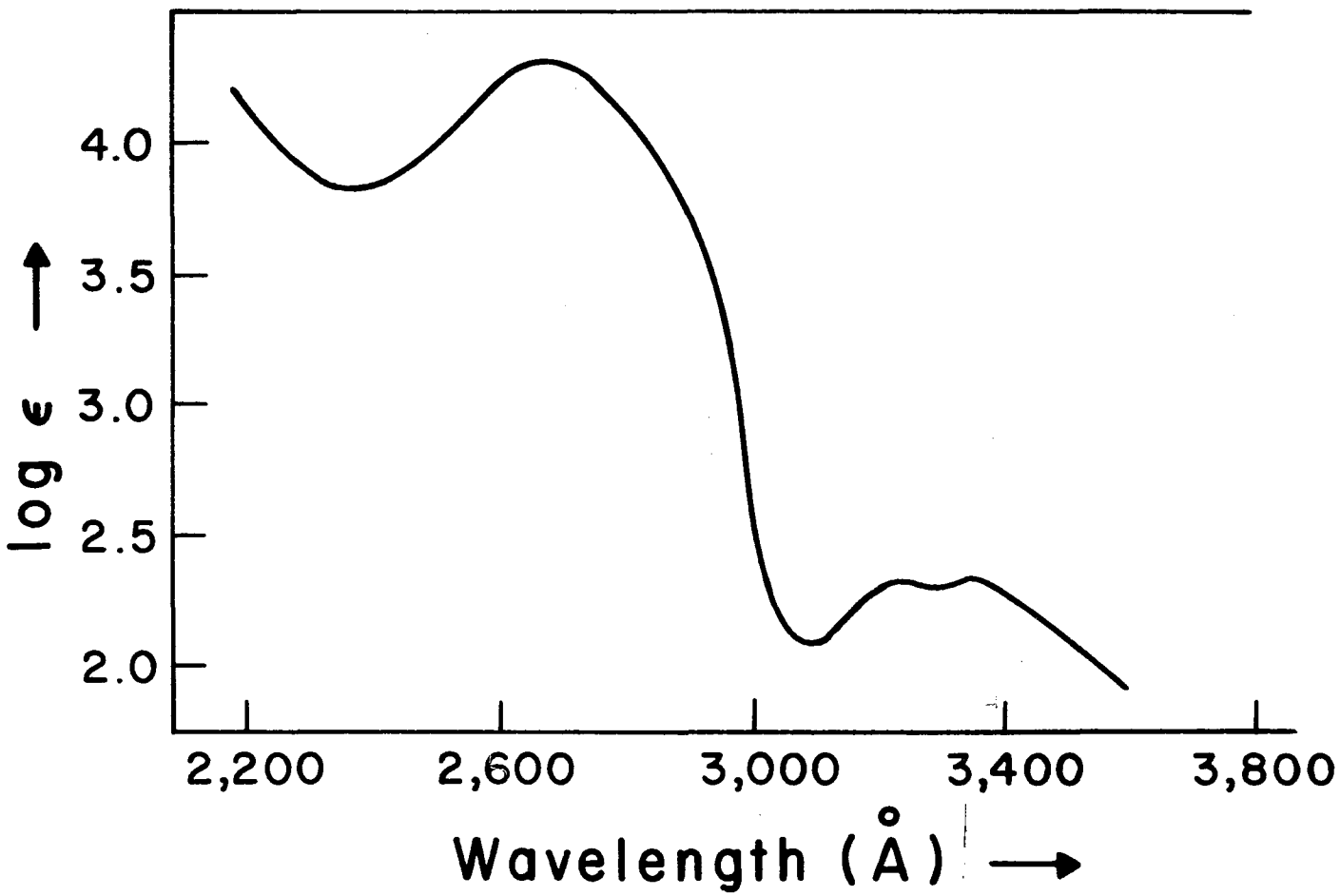

RELATIVE INTENSITY
0
1
2
3
4
5
6
7
8
9
10
200
250
300
350
WAVELENGTH (nm)

FIGURE 8. Benzophenone absorption spectrum in cyclohexane at 25° C.


4.0
3.5
3.0
2.5
2.0
log ε
2,200
2,600
3,000
3,400
3,800
Wavelength (Å)

cyclohexane solvent, yields the following results:

1) Both solvents are saturated hydrocarbons, yet there seems to be a shift toward shorter wave-lengths in the excitation spectrum.

2) The intensity ratio of the highest peak of the $\pi \rightarrow \pi^*$ transition to the highest peak of the $n \rightarrow \pi^*$ transition is about 10^2 in the absorption spectrum; the excitation spectrum yields a value of ~20.

3) There are likenesses in that the higher energy $\pi \rightarrow \pi^*$ transitions are large envelopes which show no vibrational structure while both $n \rightarrow \pi^*$ transition envelopes show some vibrational structure and have generally the same shape. The lesser relative intensity of the $\pi \rightarrow \pi^*$ band may tentatively be attributed to some quenching from a higher vibrational level of the triplet or from the singlet $\pi \rightarrow \pi^*$ state. This molecule does not exhibit any fluorescence; consequently, singlet state quenching at higher vibrational levels cannot be checked.

b) Chrysene

A good absorption spectrum of chrysene in n-heptane is presented in Figure 9. The fluorescence spectrum, Figure 10, made with the Aminco Spectrophosphorimeter is very well resolved. Figure 11 is the phosphorescence spectrum. Two excitation spectra, one as a function of fluorescence and the other as a function of phosphorescence, were made and are presented as Figures 12 and 13, respectively.

Comparison of Figures 9, 12, and 13 yields the following results:

Region	Rel. Abs. I_A	Phos. Exc. I_P	$\frac{I_P}{I_A}$	Fluor. Exc. I_F	$\frac{I_F}{I_A}$
1	44				
2	80	30	0.4	9.2	0.1
3	300	95	0.3	30	0.1
4	36	30	0.8	10	0.3
5	1	1	1	1	1

FIGURE 9. Chrysene absorption spectrum in n-heptane at 25° C. From Y. Tanaka, Bull. Chem. Soc. Jap., 38(1), 86 (1965).

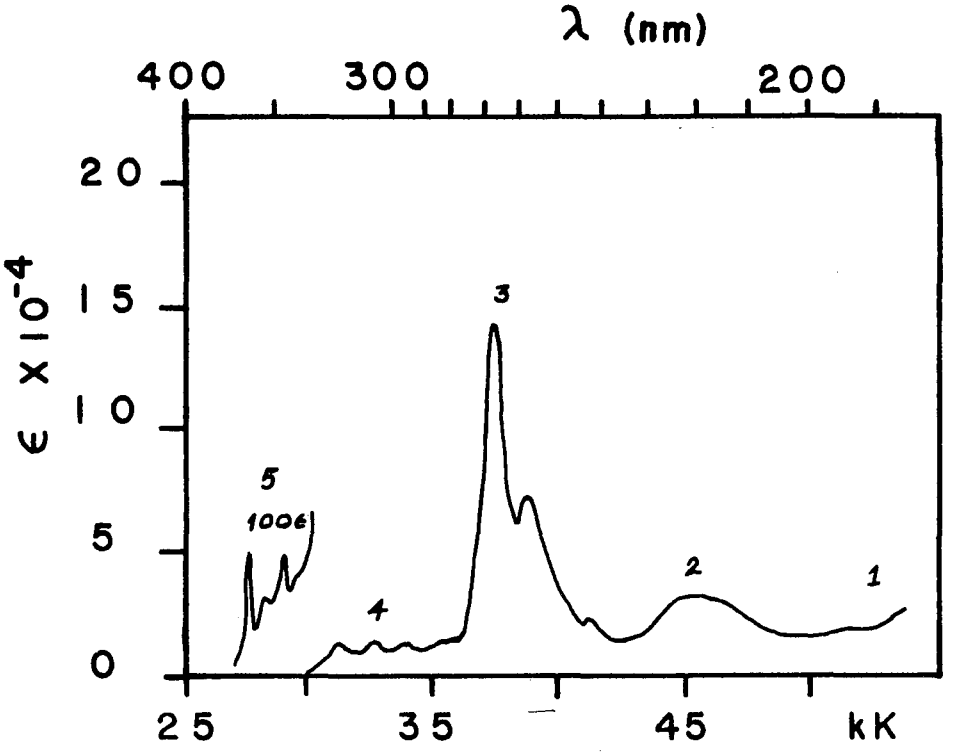

λ (nm)
400
300
200
20
15
10
5
0
ε X10⁻⁴
5
100ε
4
3
2
1
25
35
45
kK

FIGURE 10. Total luminescence spectrum of chrysene in EPA.

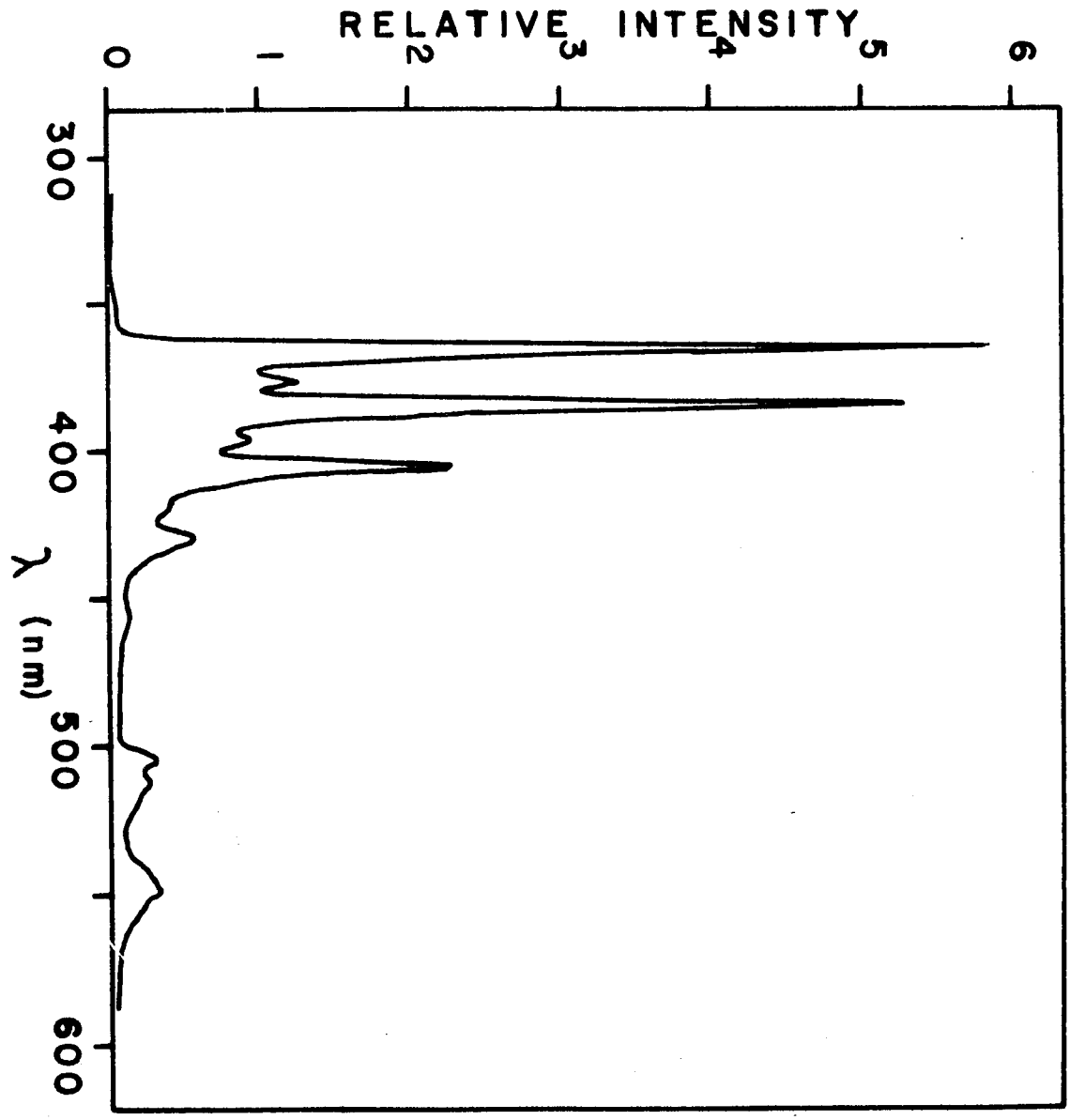

RELATIVE INTENSITY
0
1
2
3
4
5
6
300
400
500
600
λ (nm)

FIGURE 11. Phosphorescence of chrysene in EPA with poorly resolved excitation spectrum.

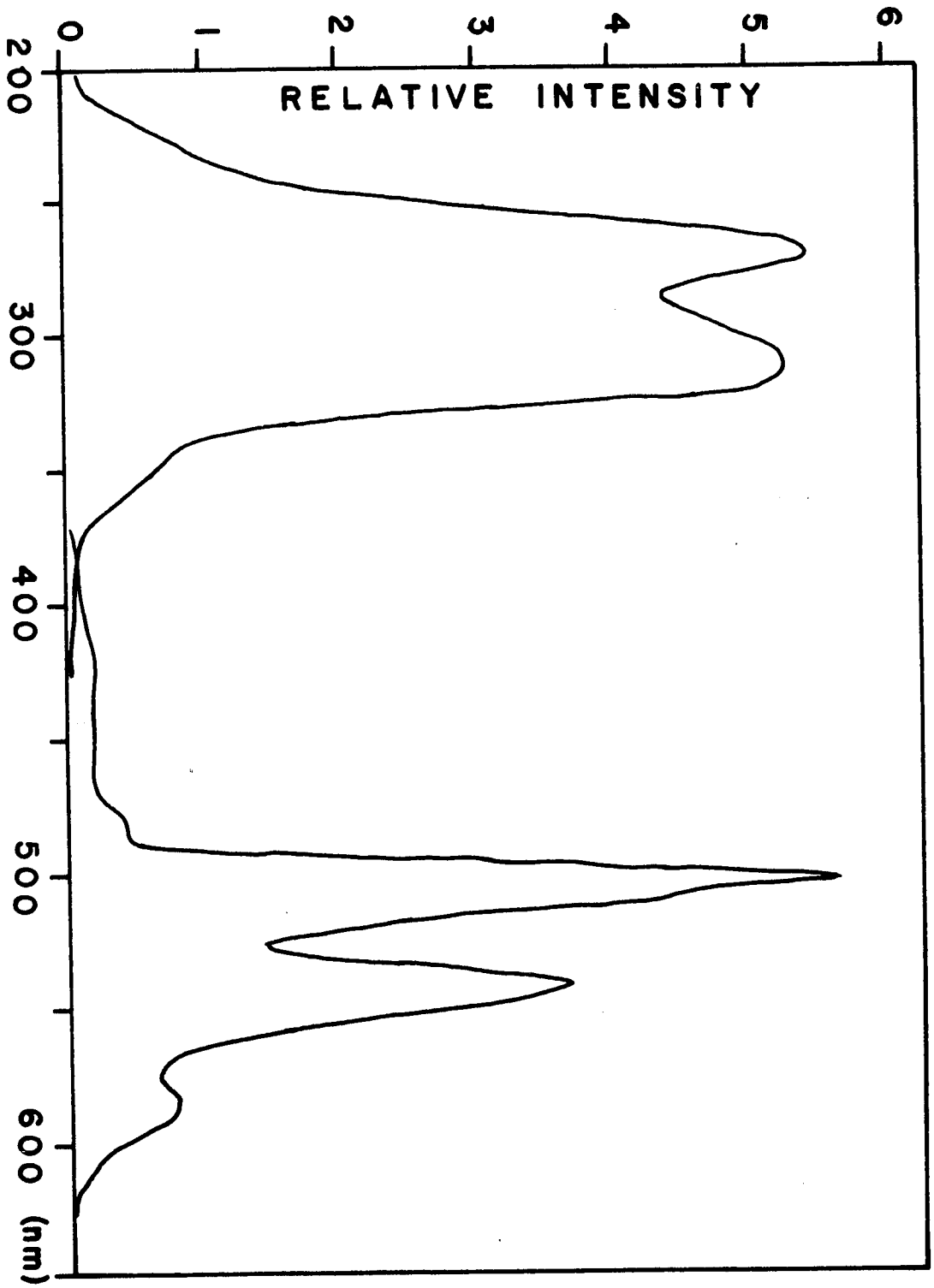

0
1
2
3
4
5
6
RELATIVE INTENSITY
200
300
400
500
600 (nm)

FIGURE 12. Corrected excitation spectrum of chrysene fluorescence.

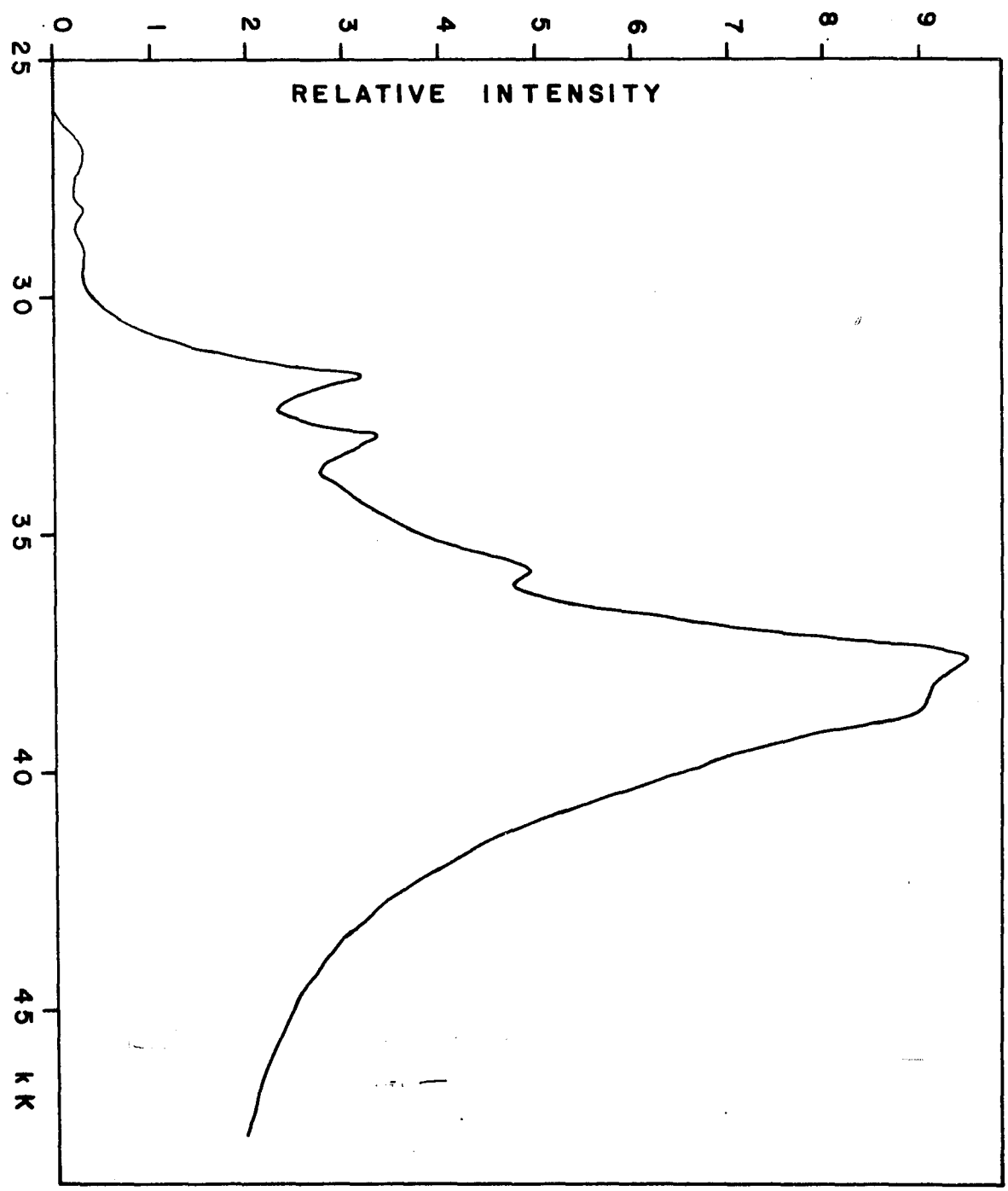
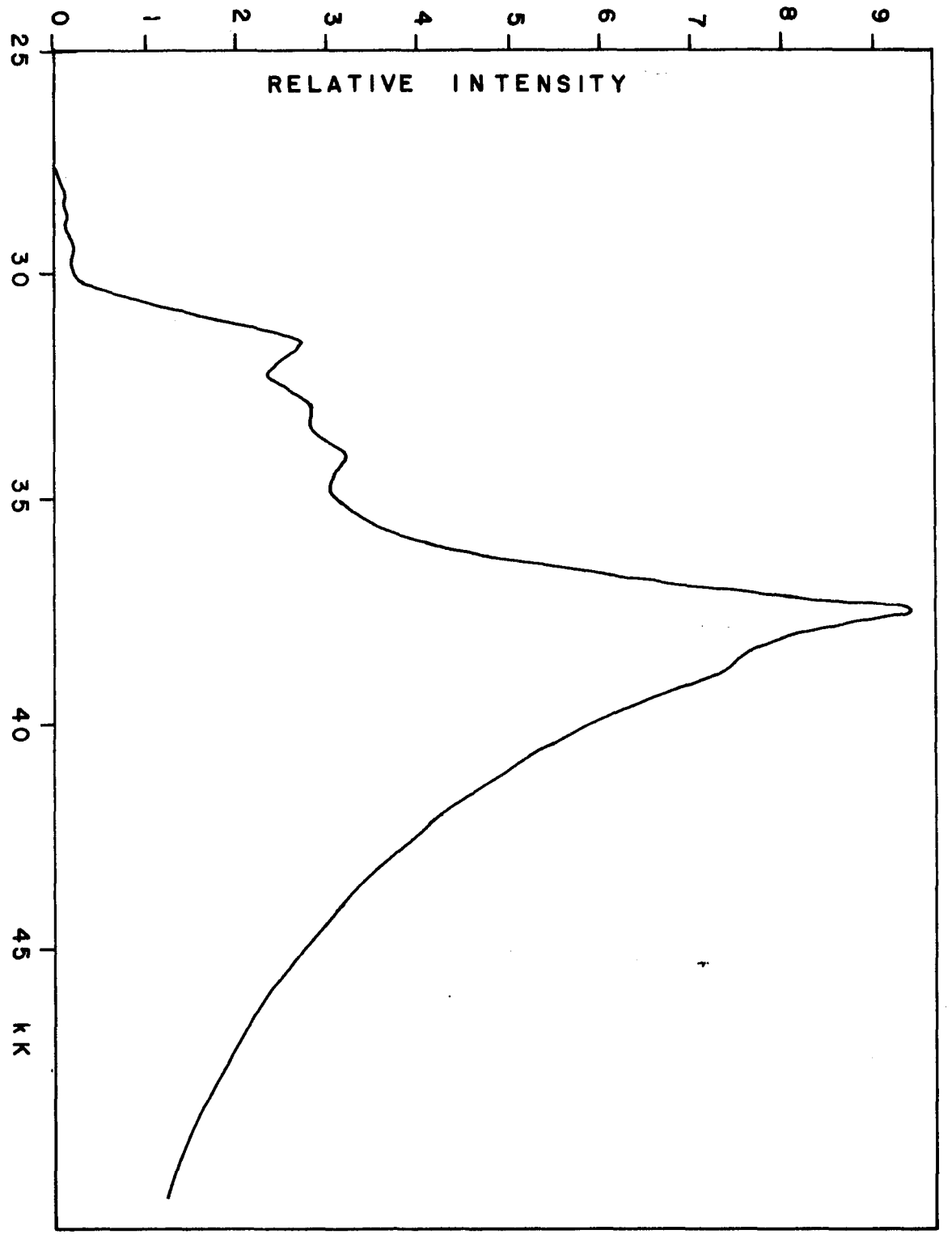

0
1
2
3
4
5
6
7
8
9
RELATIVE INTENSITY
25
30
35
40
45
kK

FIGURE 13. Corrected excitation spectrum of chrysene phosphorescence.


0
1
2
3
4
5
6
7
8
9
RELATIVE INTENSITY
25
30
35
40
45
kK

There is, apparently, considerable quenching; however, the fact that both the phosphorescence and fluorescence excitation spectra are quite similar suggests that quenching occurs mostly in the singlet manifold and little in the triplet manifold (apart from T_1). Further consideration suggests that the more probable a transition is, the less well it is replicated by an excitation spectrum. Region 2 of Figure 9 does not appear on either excitation spectrum although that wave-length region was covered. These spectra, while far from exactly replicating the absorption spectrum, do show the different electronic transitions quite well. The agreement between the two excitation spectra is remarkable and strongly indicates singlet state quenching.

c) Hexahelicene

Hexahelicene was chosen for this study because it exhibits dextro and levo helical structure. It has the structure shown in Figure 14. This structure may affect radiationless transitions from excited states to the ground state. These transitions should be reflected in an excitation spectrum which is not a replica of the absorption spectrum.

Absorption and emission spectra are shown in Figure 15. A single good emission spectrum was not obtained in the laboratory. Low temperature and room temperature absorption spectra were obtained and are shown in Figure 16.

Phosphorescence excitation was done three times; the results are shown in Figure 17. They are qualitatively very similar to the absorption spectrum. Extreme difficulty was encountered in this experiment due to unidentified luminescence, which was partly due to the filters

FIGURE 14. Structure of the aromatic molecule, hexahelicene.

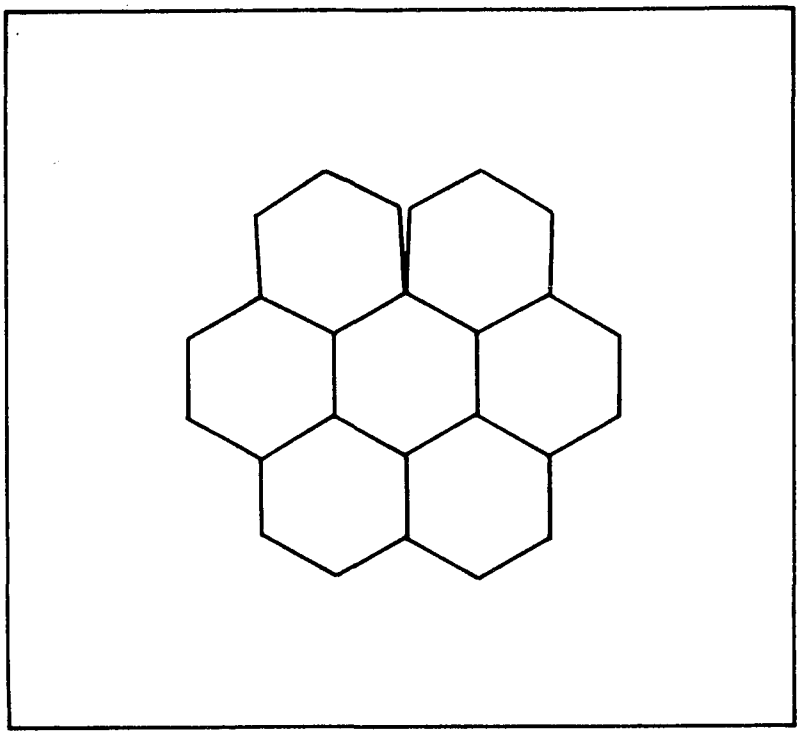


FIGURE 15. (A) Absorption spectrum of hexahelicene in diethylether at room temperature.

(B) Total emission spectrum of hexahelicene at 77° K in isopentane/methylcyclohexane (1:4). Source: Rhodes, W. and Amr El-Fayed, M. F., J. Mol. Spec., 9, 44 (1962).

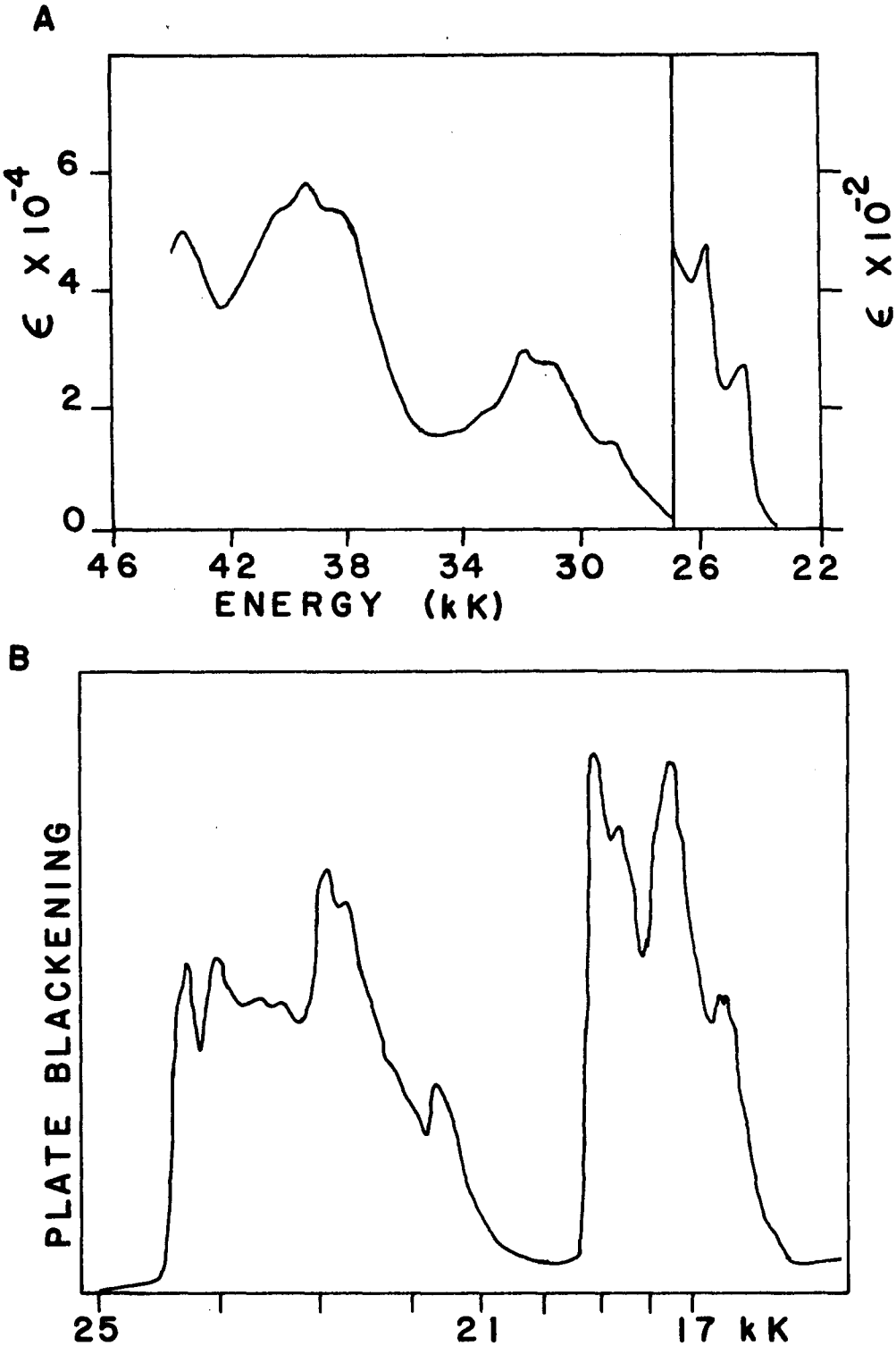

A
ε X 10^-4
6
4
2
0
ε X 10^-2
46
42
38
34
30
26
22
ENERGY (kK)
B
PLATE BLACKENING
25
21
17 kK

FIGURE 16. (A) Absorption spectrum of hexahelicene, 77° K in isopentane-3-methylpentane (6:1).

(B) Room temperature absorption spectrum in isopentane-3-methylpentane (6:1).

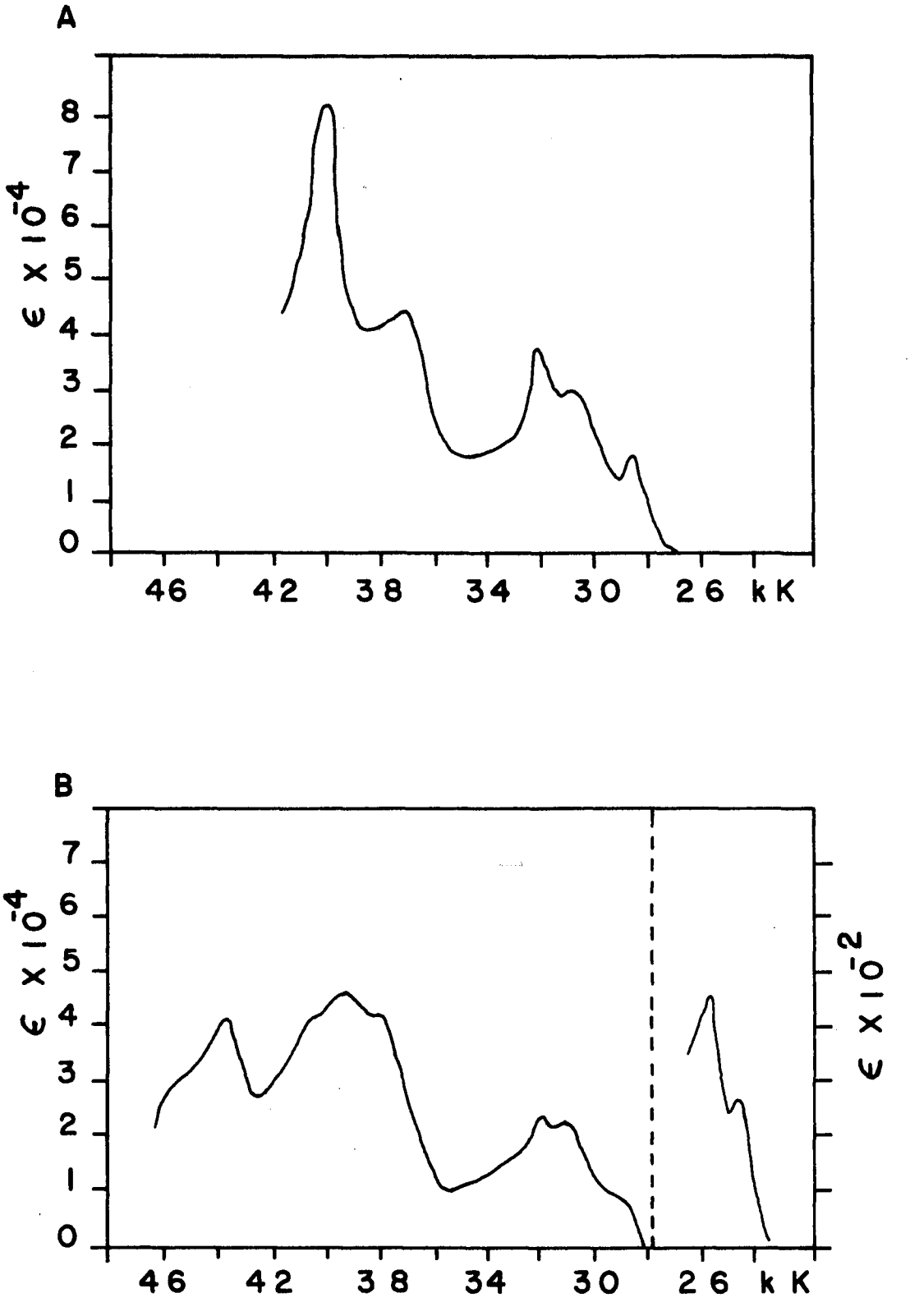
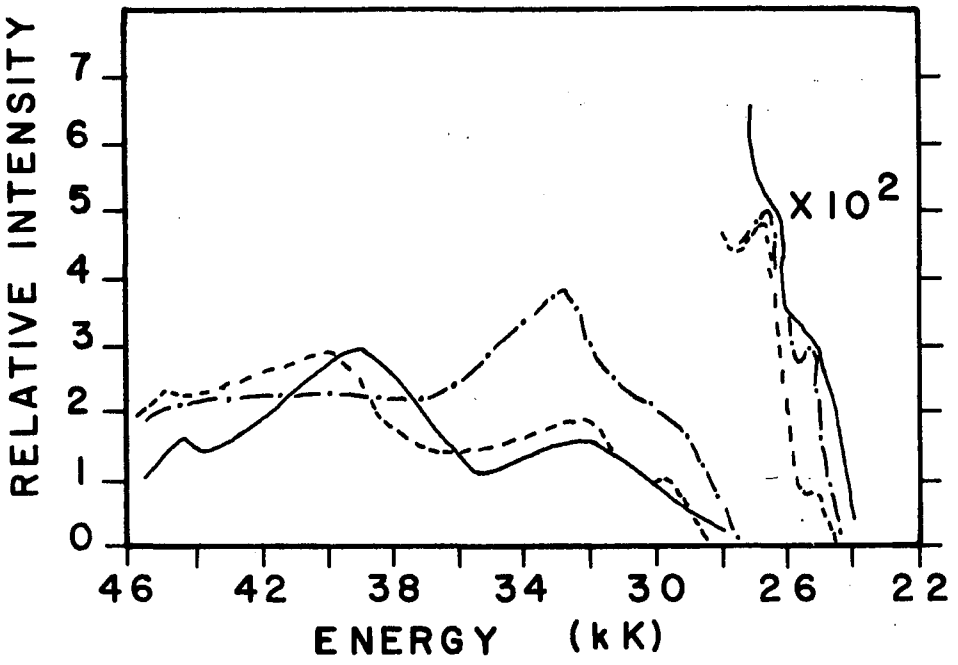

A
8
7
6
5
4
3
2
1
0
ε X 10⁻⁴
46
42
38
34
30
26
k K
B
7
6
5
4
3
2
1
0
ε X 10⁻⁴
ε X 10⁻²
46
42
38
34
30
26
k K

FIGURE 17. Corrected excitation spectrum of hexahelicene in 3-methylpentane as a function of phosphorescence at 77° K.


RELATIVE INTENSITY
0
1
2
3
4
5
6
7
X 10²
46
42
38
34
30
26
22
ENERGY (kK)

used, as well as to luminescence from impurities. The transition at an energy of ~ 28kK shows an intensity roughly 10^2 times the intensity of the band at energy lower than 28 kK.

Only one fluorescence excitation spectrum was made; it is given in Figure 18. This spectrum is not a good one; the fluorescence signal was very weak and a filter was necessary in front of the photomultiplier tube. The signal-to-noise ratio was so poor that the spectrum is almost useless. The higher energy transition exhibits up to 36 kK an intensity ratio over that of the lower energy transition of about 10^2:1. At energies higher than 36 kK no reliability can be placed on the curve.

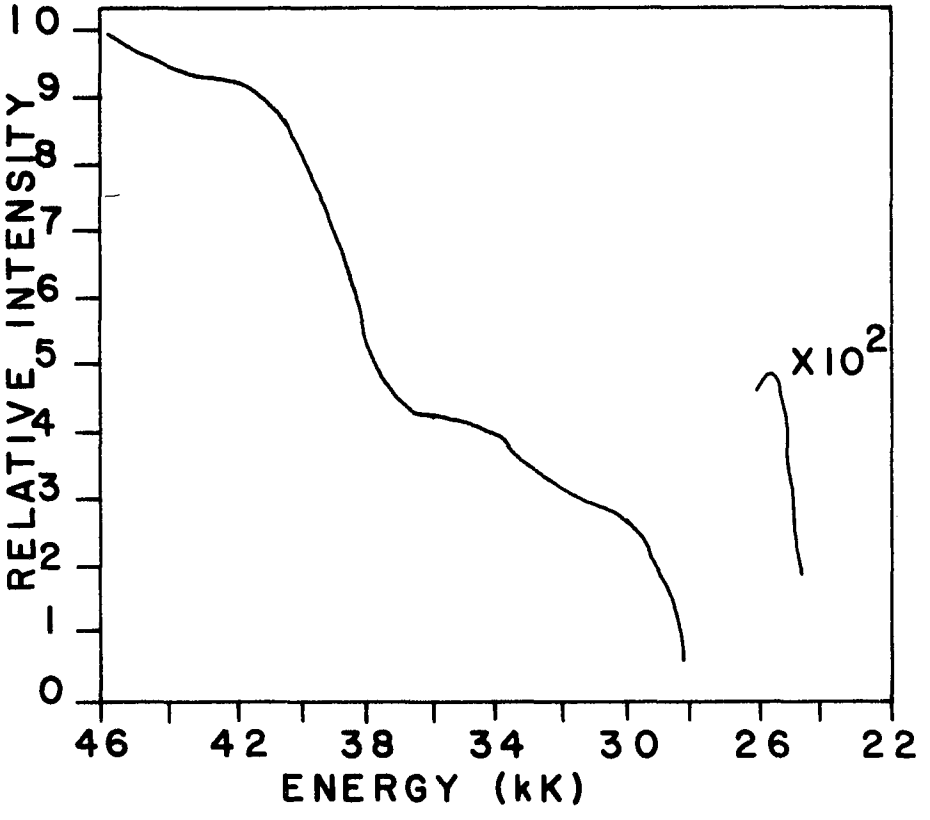
4. Conclusions

These experiments with excitation spectra have, in the main, resulted in information which, it might be said, is quite equivocal. No excitation spectrum, whether of phosphorescence or of fluorescence, exactly replicated the absorption spectrum. Some factors have interfered which caused a decrease in the excitation efficiency in the higher energy part of the absorption envelope. This may be due to external (impurity) quenching.

It is obvious that extremely careful work should be done with other very pure systems in order to gather more data from which one may deduce unequivocally whether the solute will yield an excitation spectrum which is identical to the absorption spectrum.

It may also be noted from these experiments that the excitation wavelength should not be changed when making a series of lifetime measurements on a particular solute-solvent system; this could change rates at which quenching processes occur and induce an artificial change in the measured lifetime.

FIGURE 18. Corrected excitation spectrum of hexahelicene in 3-methylpentane as a function of fluorescence at 77° K.


RELATIVE INTENSITY
0
1
2
3
4
5
6
7
8
9
10
X10²
46
42
38
34
30
26
22
ENERGY (kK)

CHAPTER II

MIXED CRYSTALS

1. Introduction

a) General

An organic mixed crystal system is a pure crystalline solid into which a certain (usually low) concentration of crystalline solute of high purity has been introduced in such a way that the solute is uniformly distributed throughout the "solvent". In practice, the solvent and solute usually consist of luminescent materials. McClure[11] employed mixed crystals in order to generate an oriented gas array of solute species for absorption studies with polarized light. Many mixed crystals also exhibit an unusual behavior in that the lifetime of one of the fluorescence components is very long lived; its lifetime, in fact, is approximately half that of the phosphorescence lifetime. This peculiar behavior is contrasted with ordinary fluorescence lifetimes which are usually in the nanosecond range. This fluorescence of anomalously long lifetime was consequently styled "delayed" fluorescence. This phenomenon was first observed by Sponer, Kanda and Blackwell,[12] and by Blake and McClure;[13] the first interpretation was provided by Nieman and Robinson.[14,15] The following explanation is now generally accepted: since phosphorescence is long-lived, delayed fluorescence must originate in kinetic events involving the triplet state; hence, the concept of triplet-triplet annihilation was developed as the necessary precursor event to the production of delayed fluorescence. Several papers[16-22] in which delayed fluorescence has been extensively studied have appeared; these have yielded much information about the phenomenon of triplet-triplet annihilation and its associated

radiationless rate constants. The radiationless rate constants, however, were not explicitly considered in any of these investigations; indeed, phosphorescence was not of any central importance to much of the work reported. In this Dissertation, phosphorescence will be of primary importance; more particularly, phosphorescence lifetime and intensity as a function of temperature will be stressed. Delayed fluorescence will be employed here only to support certain assumptions which we make about the triplet state.

b) Statement of the problem

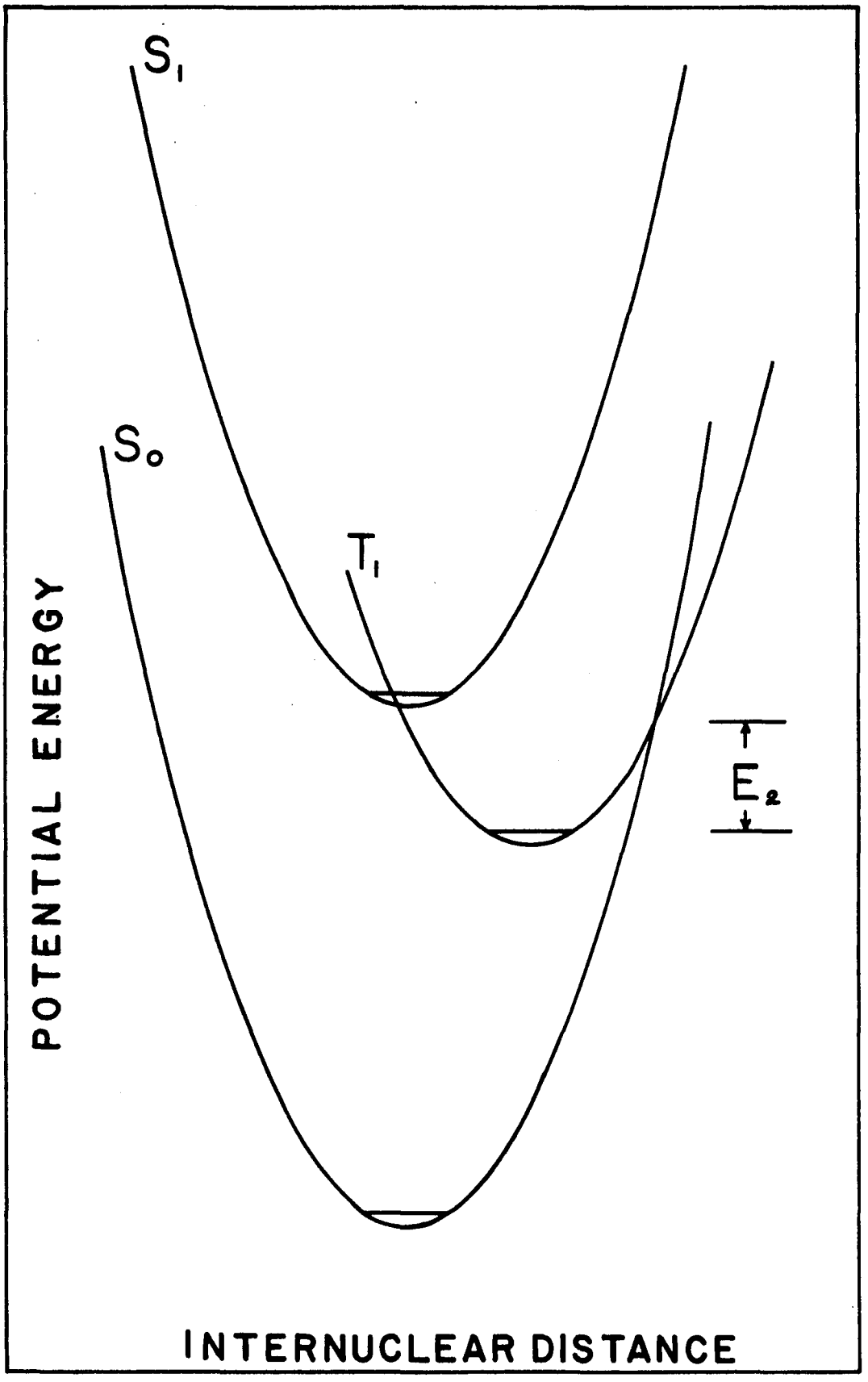
In the course of studying radiationless transitions, Hadley, Rast and Keller[23] chose to work with mixed crystal systems. Their approach to these studies was by means of the temperature dependence of the phosphorescence lifetime, for in this way they hoped to determine conclusively whether the quenching of the triplet state of the guest was an intramolecular process or an intermolecular one.

The potential energy curves necessary to the discussion of the intramolecular process are illustrated in Figure 19. If the process were intramolecular, activation from the lowest triplet state of the molecule to the ground state would involve the acquisition of a certain amount of energy, E_2, which would correspond to an integral multiple of some fundamental molecular vibrational frequency (e.g., the ring "breathing" vibration of an aromatic). The acquisition of this energy is a radiationless process; it may be subsumed into a rate equation such as the following, which Hadley, Rast and Keller used:

$$\frac{d[T]}{dt} = [S_1]\{k_1^o + k_1^a \exp(-E_1/kT)\} - [T_1]\{k_2^o + k_2^a \exp)-E_2/kT)\}, \quad (12)$$

where k_1^o is the temperature-independent rate constant from the ground

FIGURE 19. Potential energy curves for a system showing a ground singlet state, S_0, the first excited singlet state, S_1, and the lowest triplet state, T_1. E_2 is the energy difference between the cross-over point of T_1 with S_0, and the lowest vibrational level of the triplet state.


S1
S0
T1
Ea
POTENTIAL ENERGY
INTERNUCLEAR DISTANCE

vibrational level of the lowest excited singlet state to the lowest triplet state; the pre-exponential factor for the thermally activated process from the lowest excited singlet state to the lowest triplet state is given by k_1^a. Similarly, k_2^o is the temperature independent rate constant from the lowest vibrational level of the lowest triplet state. The constant, k_2^o, is the sum of the rate constant of the natural radiative decay process, k_p^N, and the triplet decay rate constant, k_4^o, for the process which depletes non-radiatively the triplet state from the lowest vibrational level of the lowest triplet state. The phosphorescence rate constant, k_p, is given by the second expression in brackets above:

$$k_p = k_2^o + k_2^a \exp(-E_2/kT). \qquad (12')$$

The quantities, E_1 and E_2, are the activation energies in the lowest excited singlet and lowest excited triplet state, respectively. The quantity E_2, more precisely, represents the difference in energy betweek the ground vibrational level of the lowest excited triplet state and the point where the lowest triplet potential energy surface meets the potential energy surface of the ground singlet state. Thus, excitation and de-excitation were presumed to occur by means of the processes shown in Table II.

Hadley, Rast and Keller[23] concluded from their experiments that the radiationless process was intramolecular, but they did not exclude the possibility that other unstated processes might occur. The thesis of this discussion is that the process which they observed is, in fact, one of the unstated processes -- that the process is intermolecular and not intramolecular. This position will be supported by sufficient experimental evidence so as to conclude rather definitely that the process is intermolecular.

TABLE II

	PROCESS	REMARKS	RATE CONSTANT
1)	$S_1 \longrightarrow S_o$	Fluorescence.	k_F
2)	$S_1 \dashrightarrow T_1$	Intersystem crossing from ground vibrational level of first excited singlet state to ground triplet state.	k_1^o
3)	$S_1^* \dashrightarrow T_1$	Thermally activated process from excited singlet state to lowest triplet state.	$k_1^a\, e^{-E_1/kT}$
4)	$T_1 \dashrightarrow\!\!\!\!\!\!\rightarrow S_o$	Decay of triplet state energy by all processes.	k_P
5)	$T_1 \longrightarrow S_o$	Phosphorescence.	k_P^N
6)	$T_1 \dashrightarrow S_o$	Radiationless decay from lowest vibrational level.	k_4^o
7)	$T_1 \longrightarrow\!\!\!\!\!\!\rightarrow S_o$	5) and 6).	$k_o^2 = k_P^N + k_4^o$
8)	$T_1^* \dashrightarrow S_o^*$	Thermal activation from ground triplet state.	$k_2^a\, e^{-E_2/kT}$
9)	$S_1 \dashrightarrow S_o$	Radiationless decay from excited singlet state to ground singlet state.	k_3^o

The kinetic scheme which is the basis for the experimental work on the luminescence of mixed crystals has been worked out by Sternlicht, Nieman and Robinson[15] and by Azumi and McGlynn.[16] The model considers a very simple system consisting of a ground singlet state, S_0, a first excited singlet state, S_1, and a lowest triplet state, T_1. A schematic drawing of the model is presented in Figure 20; the processes supposed to occur are illustrated and named. The pertinent kinetic equations will now be derived.

c) Derivation of equations

Table III lists the interaction, names that interaction or process and gives the rate constant for that process.

By employing the model illustrated in Figure 20 and using the symbols given for the rate constants, the rate equations may be written as follows:

$$\frac{d[S_1]}{dt} = R_0 - (K_1 + k_2)[S_1] + K_4[T_1]^2 \qquad (13)$$

and

$$\frac{d[T_1]}{dt} = k_2[S_1] - K_3[T_1] - (2K_4 + K_5)[T_1]^2 \qquad (14)$$

Under steady-state conditions, both equations may be set equal to zero. From (12) we may solve for $[S_1]$; this yields the equation:

$$[S_1] = \frac{R_0}{K_1 + k_2} + \frac{K_4}{K_1 + k_2}\,[T_1]^2 \qquad (15)$$

Substituting this expression for $[S_1]$ into (14), we get the following result:

$$\frac{d[T_1]}{dt} = 0 = \frac{k_2 R_0}{K_1 + k_2} + \left(\frac{k_2 K_4}{K_1 + k_2} - 2K_4 - K_5\right)[T_1]^2 - K_3[T_1] \qquad (16)$$

As a simplification for ease of writing, we let the factor

FIGURE 20. Jablonski diagram for a simple system consisting of S_0, S_1, and T_1 as in Figure 19. Arrows represent transitions and k's represent rate constants for each process.

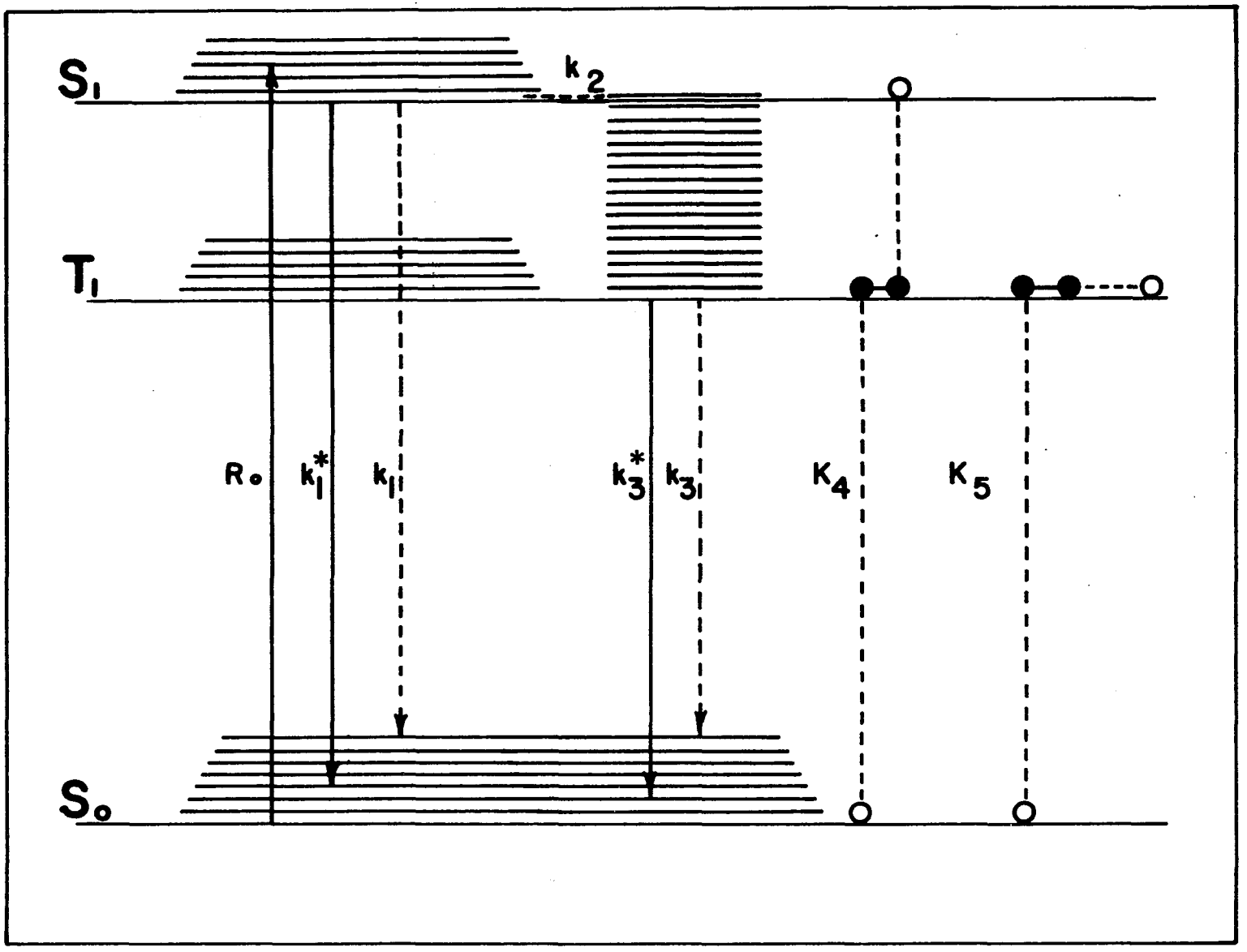

S1
k2
T1
R0
k1*
k1
k3*
k3
K4
K5
S0

TABLE III

DEFINITION OF RATE CONSTANTS AND REMARKS THEREON

	PROCESS[a]	RATE CONSTANT	REMARKS
(0)	$S_{0G}+h\nu \rightarrow S_{1G}$	R_o	Overall rate constant
(1)	$S_{1G} \rightarrow S_{0G}+h\nu_f$	k_1^*	Radiative
(1′)	$S_{1G} \rightsquigarrow S_{0G}$	k_1	Non-radiative; $K_1 \equiv k_1^*+k_1$
(2)	$S_{1G} \rightsquigarrow T_{1G}$	k_2	Intersystem crossing
(3)	$T_{1G} \rightarrow S_{0G}+h\nu_p$	k_3^*	Radiative
(3′)	$T_{1G} \rightsquigarrow S_{0G}$	k_3	Non-radiative; $K_3 \equiv k_3^*+k_3$
(4)	$T_{1G} \rightleftharpoons T_{1G}^* \rightsquigarrow T_{1H}$	$k'_{QP}\exp(-\Delta E/kT)$	Thermal activation and energy transfer
(5)	$T_{1H}+T_{1G} \rightarrow S_{0H}+T_{1G}$	K_4	Energy transfer and annihilation with another T_{1G}
(6)	$T_{1H}+T_{1G} \rightarrow S_{0H}+T_{1G}$	K_5	

a. Subscript G and H stand for guest and host, respectively.

$$\frac{k_2K_4}{K_1 + k_2} - 2K_4 - K_5 \equiv -k_6$$

The steady-state concentration of triplets is a constant for a particular system under given excitation conditions and is represented by $[T_1]_o$; therefore, before decay begins, the concentration of triplets is given by

$$[T_1]_o = \frac{K_3 \pm \left[K_3^2 + \frac{4k_2k_6R_oK_3^2}{K_3^2(K_1+k_2)}\right]^{\frac{1}{2}}}{-2k_6} \tag{18}$$

$$= \frac{K_3}{2k_6}\left[-1 \pm \left(1 + \frac{4k_2k_6R_o}{K_3^2(k_1 + k_2)}\right)^{\frac{1}{2}}\right] \tag{18'}$$

Again, for ease of expression, we let

$$\frac{k_2k_6R_o}{K_3^2(K_1 + k_2)} \equiv K. \tag{19}$$

Rewriting (18') and considering only the positive square root, we get

$$[T_1]_o = \frac{K_3}{2k_6}\left[(4K + 1)^{\frac{1}{2}} - 1\right]. \tag{20}$$

When (16) is rewritten using k_6, we have

$$\frac{d[T_1]}{dt} = \frac{k_2R_o}{K_1 + k_2} - K_3\,[T_1] - k_6[T_1]^2 \tag{16'}$$

where $[T_1]$ is the concentration of triplets after excitation cutoff and is a variable quantity. It is assumed that the excitation light is extinguished at all times greater than zero. Therefore, the behavior of R_o, the parameter which determines the rate of S_1 production <u>via</u> absorption, is given by the following expressions:

$$\begin{aligned} [T_1] &= [T_1]_o \text{ , } R_o \neq 0 \text{ when } t \leq 0; \\ [T_1] &= [T_1] \text{ , } R_o = 0 \text{ when } t \geq 0. \end{aligned} \tag{21}$$

For non-steady-state conditions when $R_o = 0$ and $t > 0$, we have the following differential equation:

$$\frac{d[T_1]}{dt} = -K_3[T_1] - k_6[T_1]^2 \tag{22}$$

Upon separation of variables, we have

$$\frac{-d[T_1]}{K_3[T_1] + k_6[T_1]^2} = dt \tag{23}$$

From a table of integrals, we see that

$$\int \frac{dx}{x(a + bx)} = -\frac{1}{a} \ln \frac{a + bx}{x} \tag{24}$$

We apply this result to (22) and we get the following definite integral with the help of (21):

$$\ln \frac{K_3 + k_6[T_1]}{[T_1]} \Bigg|_{[T_1]_o}^{[T_1]} = K_3 t \Big|_o^t \tag{25}$$

The boundary conditions are:

$[T_1] = o$, when $t = \infty$,

$[T_1] = [T_1]_o$, when $t = o$

Completing (25), we get

$$\ln \left[\frac{K_3 + k_6[T_1]}{[T_1]} \cdot \frac{[T_1]_o}{K_3 + k_6[T_1]_o}\right] = K_3 t \tag{26}$$

Expressing (26) in exponential form, we have

$$\frac{K_3 + k_6[T_1]}{[T_1]} \cdot \frac{[T_1]_o}{K_3 + k_6[T_1]_o} = \exp (K_3 t) \tag{27}$$

We may now let

$$\frac{k_6[T_1]_o}{K_3 + k_6[T_1]_o} \equiv A \tag{28}$$

Multiplying both sides by $\frac{K_3}{k_6}$, we get the following result:

$$\frac{K_3}{k_6} A = \frac{K_3[T_1]_o}{K_3 + k_6[T_1]_o} = \frac{K_3}{K_3 + k_6[T_1]_o} \qquad [T_1]_o = (1 - A)[T_1]_o \tag{29}$$

If (27) is multiplied by $\frac{k_6}{k_6}$, we get the following result:

$$\frac{K_3 + k_6[T_1]}{k_6[T_1]} \cdot \frac{k_6[T_1]_o}{K_3 + k_6[T_1]_o} = \exp(K_3 t) \tag{30}$$

Substituting (28) into (30), we get:

$$\frac{K_3 + k_6[T_1]}{k_6[T_1]} A = \exp(K_3 t) \tag{31}$$

By factoring $\frac{1}{[T_1]}$ from (31), we have

$$\frac{1}{[T_1]} \left(\frac{K_3}{k_6} A + A[T_1]\right) = \exp(K_3 t) \tag{32}$$

From (29) we may substitute for $\frac{K_3}{k_6} A$:

$$\frac{1}{[T_1]} \{(1 - A)\ [T_1]_o + A[T_1]\} = \exp(K_3 t) \tag{33}$$

Algebraic manipulation yields the following result:

$$\frac{[T_1]}{[T_1]_o} = \frac{1 - A}{\exp(K_3 t) - A} \tag{34}$$

Since the intensity of phosphorescence is directly proportional to the concentration of triplets in the system we may rewrite (34) in the following manner:

$$\frac{[T_1]}{[T_1]_o} = \frac{1 - A}{\exp(K_3 t) - A} = \left(\frac{I}{I_o}\right)_p \tag{35}$$

It is desirable to do this since the intensity of phosphorescence is a measurable quantity, whereas the concentration of triplets is not.

It is interesting to show how K, as defined in (19), is related to A, as defined in (28). Rewriting (28), we have:

$$A = \frac{k_6[T_1]_o}{K_3 + k_6[T_1]_o} ; \tag{28^1}$$

Upon rearranging (28), we get

$$K_3 A + k_6 A[T_1]_o = k_6[T_1]_o, \tag{36}$$

or,

$$\frac{K_3}{k_6} A + A[T_1]_o = [T_1]_o \tag{37}$$

We now substitute the quantity for $[T_1]_o$ from (20) with the following result, after cancellation of common factors:

$$A + \frac{A}{2} (\sqrt{4K + 1} - 1) = \frac{1}{2} (\sqrt{4K + 1} - 1) \tag{38}$$

Multiplying through by 2, we have

$$2A + A (\sqrt{4K + 1} - 1) = \sqrt{4K + 1} - 1 \tag{39}$$

We may simplify the left-hand side to find:

$$A (\sqrt{4K + 1} + 1) = \sqrt{4K + 1} - 1 \tag{40}$$

Solving for A, we get

$$A = \frac{\sqrt{4K + 1} - 1}{\sqrt{4K + 1} + 1} \tag{41}$$

We have now shown how the parameter A is related to the parameter K.

Thus far we have considered only triplet state decay. Turning to (13), we have

$$\frac{d[S_1]}{dt} = R_o - (K_1 + k_2)[S_1] + K_4[T_1]^2 \tag{13'}$$

At the moment of excitation cut-off, we have $R_o = 0$; since normal fluorescence is very short-lived, $\frac{d[S_1]}{dt}$ very quickly becomes zero after excitation cut-off, so that we have the following result from (13):

$$[S_1] = \frac{K_4}{K_1 + k_2} [T_1]^2 \tag{42}$$

After normal fluorescence has decayed, the fluorescence which is still observed is due to triplet-triplet annihilation. For this reason, we conclude that the intensity of the residual fluorescence (delayed fluorescence) is proportional to the concentration of triplets squared:

$$I_{DF} \propto [T_1]^2 \tag{43}$$

We may then set up a ratio to eliminate the constants of (42) while substituting for $\frac{[T_1]}{[T_1]_o}$:

$$\left(\frac{I}{I_o}\right)_{DF} = \frac{(1 - A)^2}{[\exp(K_3 t) - A]^2} \tag{44}$$

The equation of most importance in this work is (35), which states that

$$\left(\frac{I}{I_o}\right)_P = \frac{1 - A}{\exp(K_3 t) - A} \tag{35'}$$

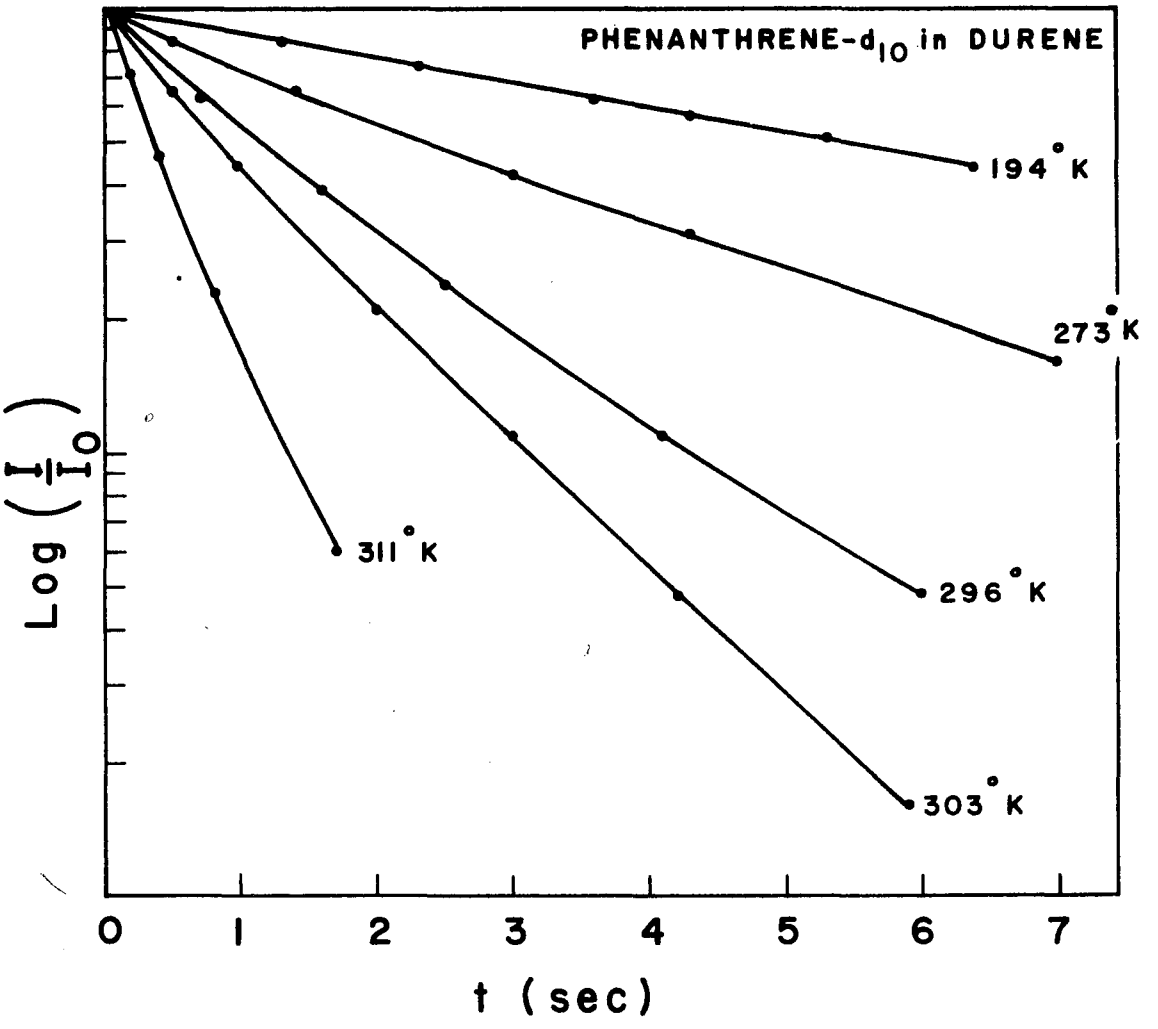
The parameter, A, is a measure of the contribution of the second-order term of (14) to the rate of decay of the triplet state concentration. The second-order term is concerned solely with triplet-triplet annihilation. When there is no annihilation processes, k_6 equals zero and, consequently, the parameter A equals zero also, so that

$$\left(\frac{I}{I_o}\right)_P = \exp(-K_3 t) \tag{45}$$

If log $\left(\frac{I}{I_o}\right)_P$ plotted <u>versus</u> time, a straight line should result, the slope of which is $-K_3$. Only at lower temperatures is the decay curve straight for all values of t. After excitation cut-off, A quickly approaches zero so that (45) is still valid. This is true even at higher temperatures where the annihilative process is very active.

Figure 21 shows that straight lines do result. This fact allows the experimenter to use phosphorescence decay and therefore K_3 at higher temperatures if that portion of the phosphorescence decay curve is used where (35) closely approximates (45). This is experimentally realized in the longer-term region of the curves of Figure 21.

FIGURE 21. Log $\left(\frac{I}{I_o}\right)_p$ plotted against time for various temperatures. Temperature increases downward.


PHENANTHRENE-d_{10} in DURENE
194°K
273°K
296°K
303°K
311°K
$\log\left(\frac{I}{I_0}\right)$
0
1
2
3
4
5
6
7
t (sec)

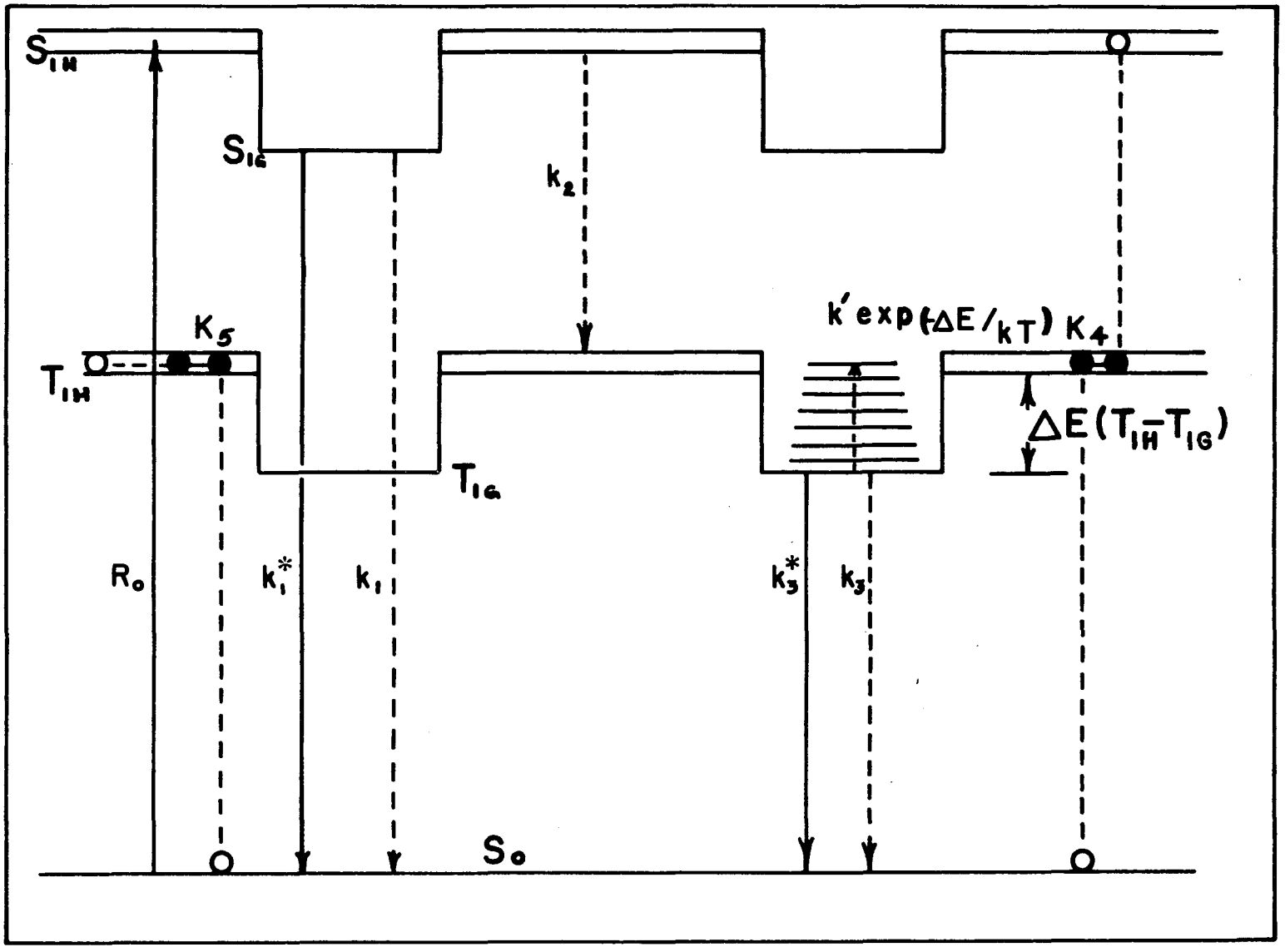
d) Discussion of models and processes

The model illustrated by Figure 20, which shows the various processes necessary to this mathematical development, is probably oversimplified; it is not strictly applicable to mixed crystal systems, for in such systems many more processes assuredly occur. However, the kinetic derivation considers only those rate determining processes which we have already specified. States higher than the first excited state of a given multiplicity manifold are assumed to degrade very fast to the lowest excited state of that manifold. This is assumed to be such a fast process that it has no effect on the kinetic development. To visualize the larger number of processes involved in a mixed crystal, a more detailed model is required; such a model is given by Figure 22.

In order to be able to proceed with the discussion of mixed crystal systems a new notation convention must be introduced. The model illustrated by Figure 22 considers more energy levels than does Figure 20. These levels will now be explained. The lowest level for this system is designated S_O and is the common ground state for both host and guest aromatic species. The symbol T_{IG} is the lowest triplet state of the guest. It is not an exciton band; it is rather a "trap" which exists due to a discontinuity in the host triplet exciton band. The host triplet exciton band is designated T_{IH}. Similarly, S_{IG} refers to the discontinuity in the exciton band of the lowest singlet state of the host; this forms a lowest singlet trap of the guest aromatic. The symbol S_{IH} refers to the exciton band of the lowest singlet state of the host.

The initial excitation of the mixed crystal is usually arranged so as to produce molecules whose energy state is in the singlet host

FIGURE 22. Exciton bands for host singlet state and host triplet state are shown; the "traps" are due to guest "impurities". Transitions are shown along with corresponding rate constants.


S_{1H}
S_{1G}
k_2
$k' \exp(-\Delta E/kT)$
K_4
K_5
T_{1H}
$\Delta E (T_{1H} - T_{1G})$
T_{1G}
R_0
k_1^*
k_1
k_3^*
k_3
S_0

exciton band. The energy in this band then redistributes itself as follows: it may transfer radiationlessly to the singlet guest level, whence it may further decay radiationlessly to the triplet guest level. The T_{IG} exciton may now undergo a radiative phosphorescence event, or it may engage in an annihilative process with another guest triplet exciton. The anihilative process can result in either the simultaneous production of S_{OG} and S_{IG} states, or of S_{OG} and T_{IG} states. The annihilatively produced S_{IG} state may emit radiation or degrade radiationlessly; the annihilatively produced triplet exciton may engage again in annihilation with another triplet exciton.

There is a distinct possibility that S_{IH} may degrade into T_{IH} by an intramolecular pathway. This triplet exciton, T_{IH}, may degrade further to S_{OH}; it may also migrate within the host triplet band until a guest triplet trap is encountered, whereupon it is trapped. The events described in the previous paragraph may again ensue in normal fashion.

In such a mixed crystal system, temperature has an important and even critical determinative effect on the probability with which the various processes may occur. At relatively low temperature, exciton migration within the host triplet band is not very efficient; trapping at guest sites is a much too probable event. Once this exciton is trapped, its escape into the host exciton band is virtually impossible because of the inadequacy of the available thermal energy. Consequently, S_{OG} is achieved by exothermic intramolecular pathways.

With these variations of the kinetic model in mind, the mathematical expression for the triplet state decay rate constant may be reexamined. Instead of using the rate constants of Hadley, Rast and

Keller, we shall now use those of Figure 22 and Table III. From these two sources we see that K_3 is the sum of k_3^* and k_3. It has been established in (45) and in the following discussion that K_3 may be used even at higher temperatures, but this value must be taken from the longer time region of the phosphorescence decay curve. Since K_3 is the sum of a radiative process and a non-radiative process, for a mixed crystal system it may be modified to the following:

$$K_3 = k_3^* + k_3 \exp(-\Delta E/kT) \qquad (46)$$

In terms of the thesis of this paper, ΔE, as is seen from Figure 22, represents the energy difference between the lowest energy triplet level of the host species and the lowest energy triplet level of the guest species. To prove the thesis that the process is in fact intermolecular, a number of binary systems representing a rather large range of ΔE values should be studied.

Now that the kinetic development is well established, we may work with phosphorescence decay. We again change notation in the sum of rate constants to conform to the names which we give to the process. We have then,

$$k = k_P + k_{QP}(T) = k_P + k_{QP}^o + k_{QP}' \exp(-\Delta E/kT) \qquad (47)$$

Here, k_P is the decay rate constant for the emissive $T_{IG} \rightarrow S_{OG}$ process and $k_{QP}(T)$ is the temperature dependent non-emissive part of the decay process. The temperature dependent part is further considered to be separable into two terms: k_{QP}^o, which is temperature independent; and the second term, $k_{QP}' \exp(-\Delta E/kT)$ which consists of two factors, k_{QP}'; a pre-exponential rate constant which is modified by $\exp(-\Delta E/kT)$; ΔE is the guest triplet-host triplet energy difference.

The employment of equation (47) is valid only when triplet state energy is considered to be transferred very fast from the host to the guest species. Host processes, therefore, are not explicitly represented in our kinetic considerations.

The use of equation (47) does not affect any of the previously derived results. We have applied the equation in the following manner to the data collected in the laboratory: in the region where $(I/I_o)_p = \exp(-K_3 t)$ is approximately valid, as discussed previously,* the terms $k_p + k^o_{QP}$ are assumed to be the triplet state decay rate constant at 77° K and are denoted by k_o. We have now

$$k = k_o + k'_{QP}\exp(-\Delta E/kT) \tag{48}$$

Since $k \equiv \frac{1}{\tau}$, where τ is the lifetime of the phosphorescence, we may rewrite (37), getting

$$\frac{1}{\tau} = \frac{1}{\tau_o} + \frac{1}{\tau^I}\exp(-\Delta E/kT) \tag{49}$$

Simple manipulation, followed by taking the logarithm of both sides, yields

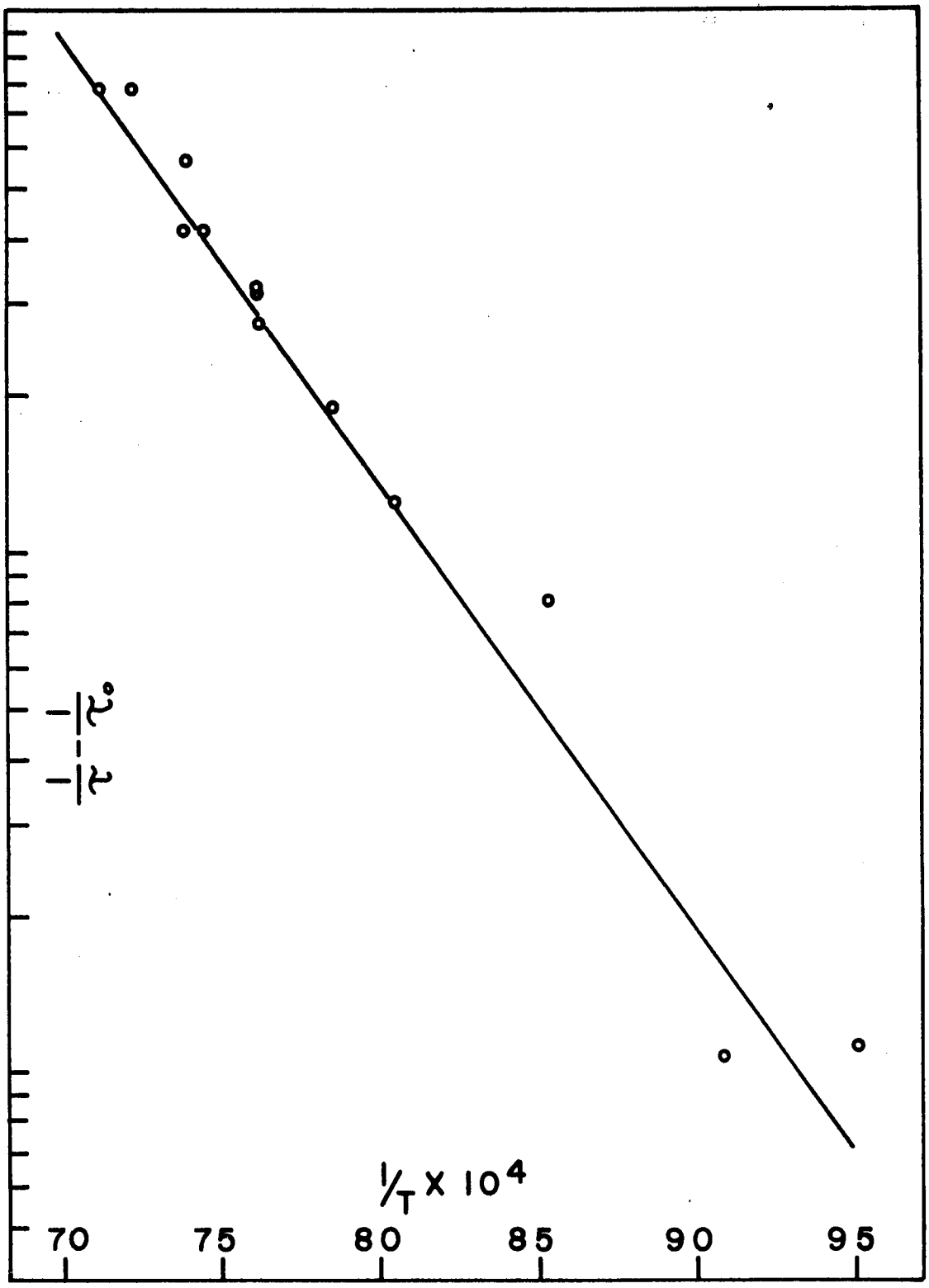
$$\ell n\left(\frac{1}{\tau} - \frac{1}{\tau_o}\right) = \ell n \frac{1}{\tau^I} - \Delta E/kT \tag{50}$$

Because of (45) we may find K_3 (or k because of (48)). Having k we may find τ and make graphs <u>versus</u> temperature for a particular system under study. Taking experimental points from these graphs and making an Arrhenius plot (logarithm of some quantity plotted <u>versus</u> the reciprocal of the temperature at which that quantity was measured), we see that we may find the quantity $-\Delta E/k$ as the slope of that plot. Such a plot is shown in Figure 23.

---

*Note that $K_3 = k = k_p + k_{QP}(T) = k_p + k^o_{QP} + k'_{QP}\exp(-\Delta E/kT)$

FIGURE 23. Mixed crystal system: phenanthrene-d_{10} in biphenyl. Arrhenius plot of $\log \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$ versus $\frac{1}{T}$. The slope yields $\Delta E/k$.


$\frac{\partial^2}{\partial z^2}$
$1/T \times 10^4$
70
75
80
85
90
95

In this manner the data from the eleven systems chosen were analyzed in an attempt to estimate the relative intermolecular nature of the temperature dependence of mixed crystal phosphorescence decay when the guest triplet state is of lower energy than the host triplet state.

2. Experimental

a) Chemicals and apparatus

All materials used were recrystallized from an appropriate solvent system. They were then zone refined; the zone refining process was carried out to the extent that each host and guest sample underwent at least one hundred melting and solidification cycles. The guest species was mixed into the host species by means of an agate mortar and pestle; the guest concentration was one mole percent in all cases. Considerable care was exercised while mixing the two species: high crushing pressures exerted by the pestle produce quite high temperatures which can lead to both decomposition and oxidation, thereby introducing undesirable impurities.

The crystals used in these studies were grown slowly from the melt between quartz plates of dimensions 1 cm x 2 cm. The crystal spectra were recorded by means of an Aminco-Keirs Spectrophosphorimeter. The same instrument was used in the temperature dependence work. All spectra and phosphorescence decay curves were recorded on an Electric Instruments X-Y recorder.

b) Temperature control

To vary the temperature of the mixed crystals, gaseous nitrogen was boiled off the liquid and was conducted through an insulated tube

to a copper coil which was immersed in liquid nitrogen. The temperature in the sample compartment was regulated by the rate of flow of the nitrogen gas. A Variac was used to regulate the rate of boil-off and thus the rate of flow of nitrogen gas.

c) Temperature measurement

The temperature was monitored continuously by means of a copper-constantan thermocouple connected to a Sargent SR recorder. One junction of the thermocouple was held at the temperature of liquid nitrogen; the other was in contact with one of the quartz plates which held the sample. The temperature was recorded indirectly as recorder pen displacement; a standard curve based on the melting points of common laboratory liquids was used to convert the recorder pen displacement to temperature.

d) Lifetime measurement

Measurements of phosphorescence lifetime were made when the recorder indicated a constant temperature and when the phosphorescence intensity held a steady value, for in some systems the phosphorescence intensity changed although there was no perceptible change in the temperature.

3. Results and Discussion

a) Review of graphs with discussion

Graphs of the phosphorescence lifetimes as a function of temperature are presented in Figures 24 through 29. In order to make the Arrhenius plots, experimental points were used for the lifetimes and temperatures of (50). The symbol, τ_0, represents the lifetime of the phosphorescence at 77° K. The Arrhenius plots previously mentioned

FIGURE 24. Mixed crystal system: naphthalene in durene and in biphenyl. Graph of lifetime versus temperature.

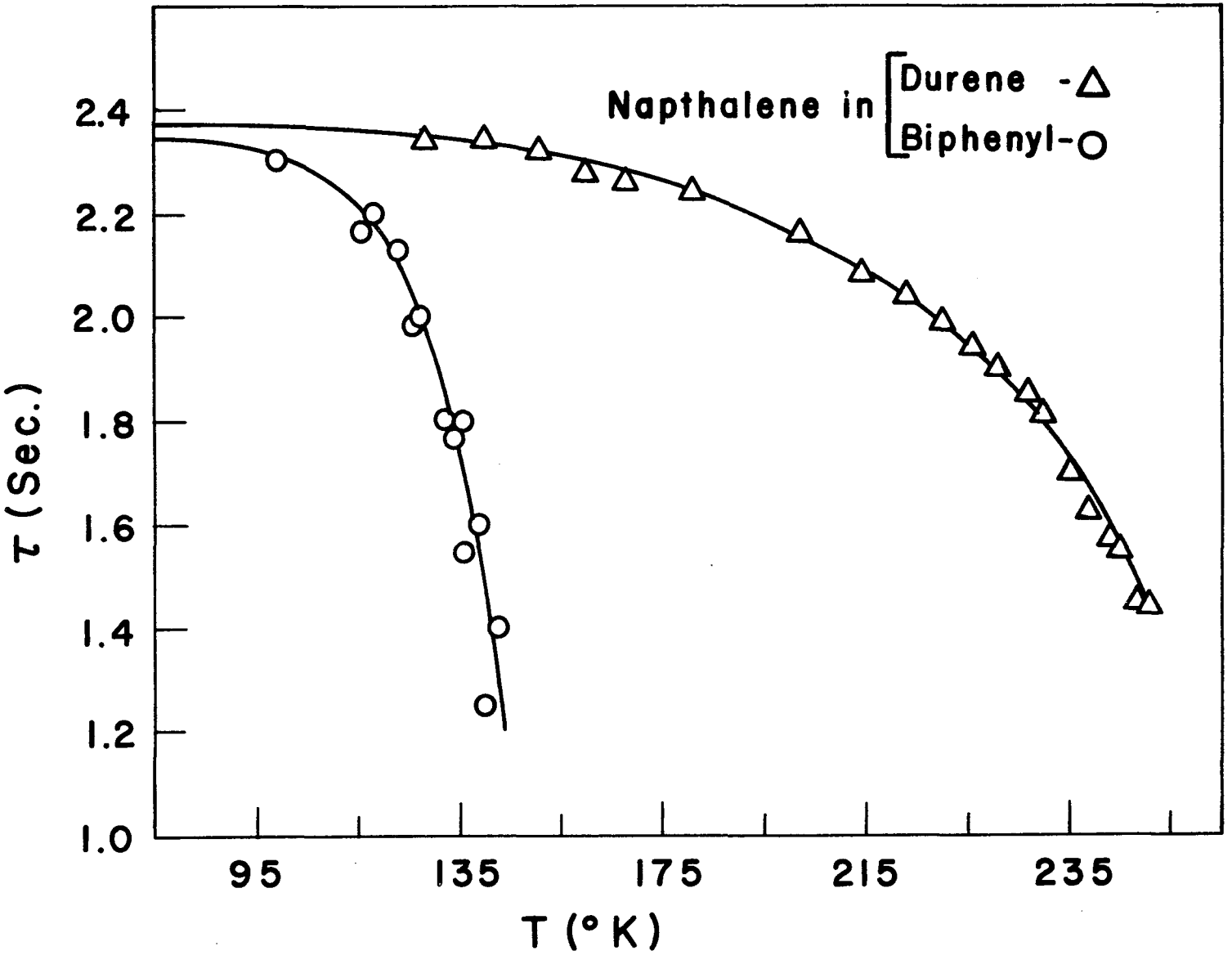

Napthalene in
Durene -△
Biphenyl-○
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
τ (Sec.)
95
135
175
215
235
T (° K)

FIGURE 25. Mixed crystal system: naphthalene-d_8 in durene and in biphenyl. Graph of lifetime versus temperature.

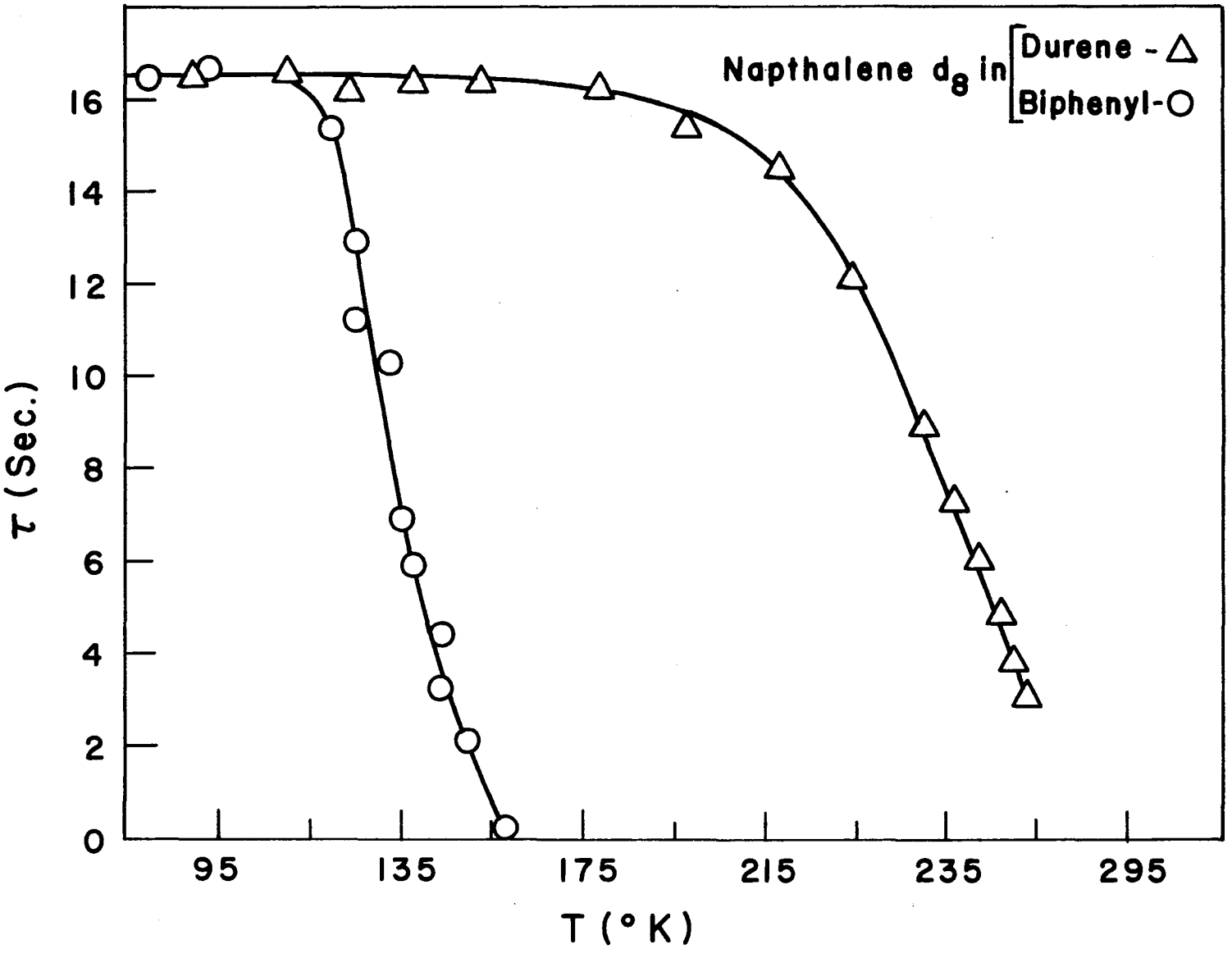

Napthalene d_8 in
Durene - △
Biphenyl - ○
τ (Sec.)
0
2
4
6
8
10
12
14
16
95
135
175
215
235
295
T (° K)

FIGURE 26. Mixed crystal system: chrysene in durene and in biphenyl. Graph of lifetime versus temperature.

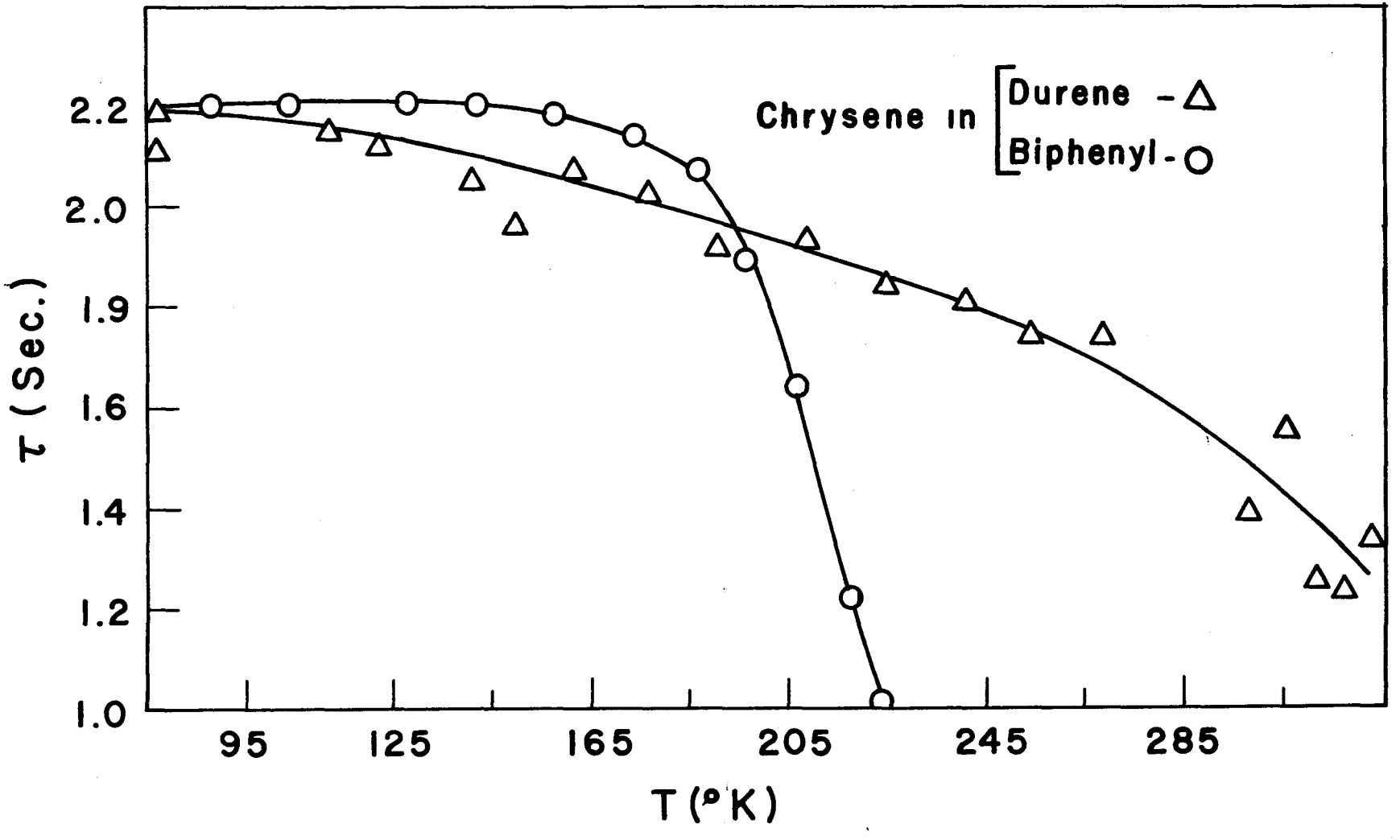

Chrysene in
Durene - △
Biphenyl - ○
τ (Sec.)
2.2
2.0
1.9
1.6
1.4
1.2
1.0
95
125
165
205
245
285
T (°K)

FIGURE 27. Mixed crystal system: phenanthrene-d_{10} in durene and in biphenyl. Graph of lifetime versus temperature.

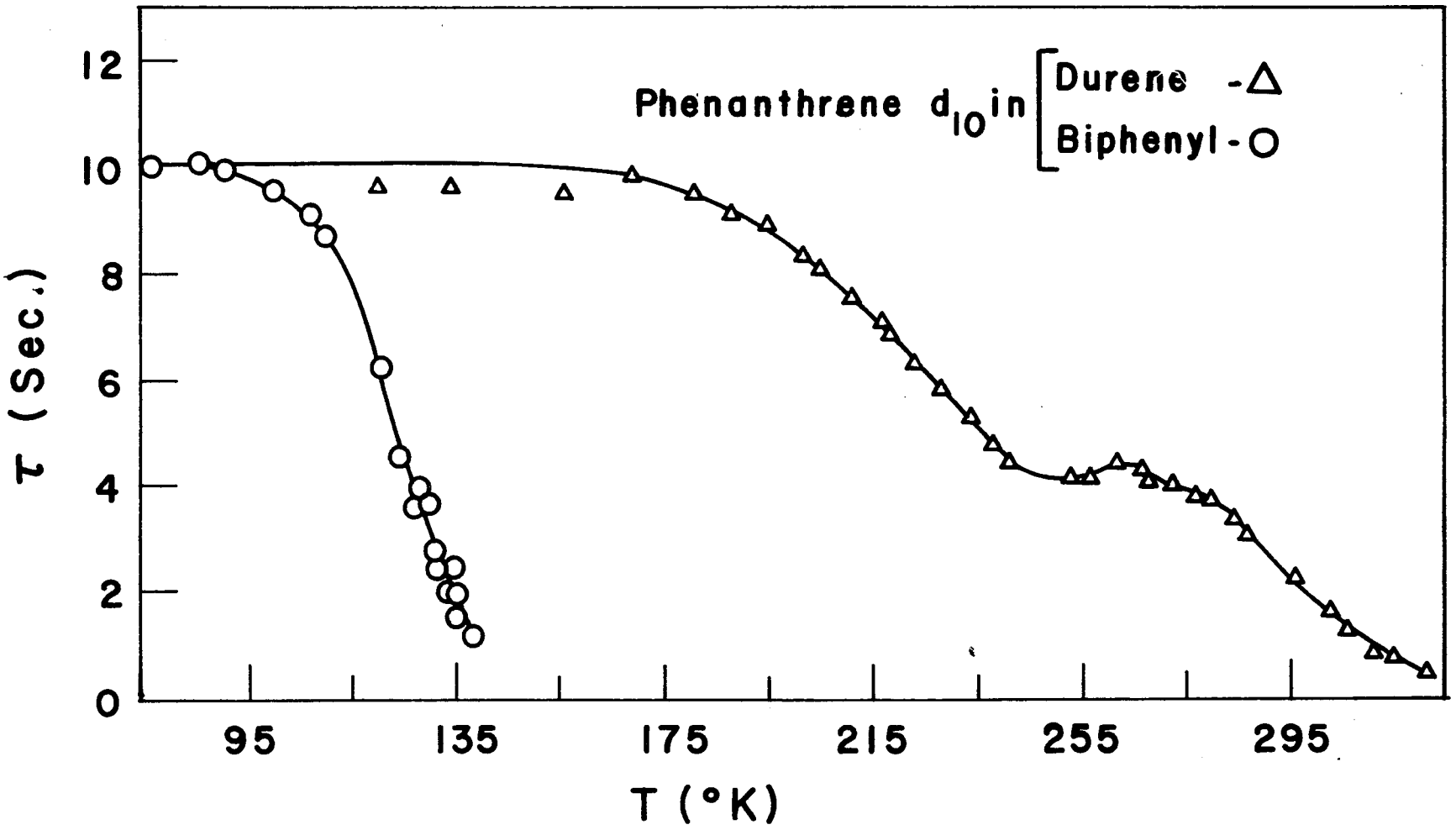

Phenanthrene d_{10} in [Durene -△ Biphenyl -○
τ (Sec.)
T (°K)
0
2
4
6
8
10
12
95
135
175
215
255
295

FIGURE 28. Mixed crystal system: phenanthrene in durene and in biphenyl. Graph of lifetime versus temperature. Phenanthrene in biphenyl (open circles), phenanthrene in durene (filled circles).

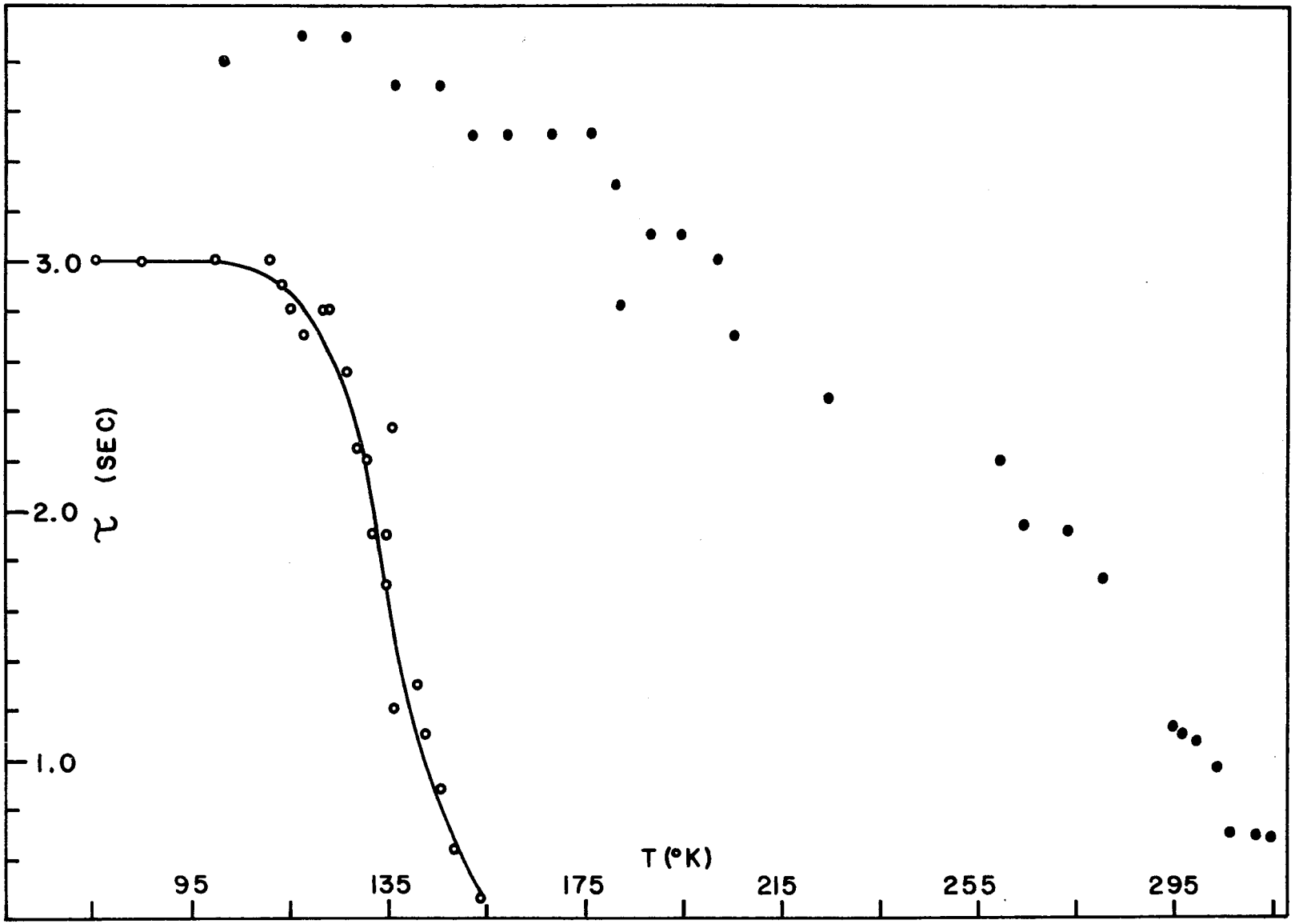
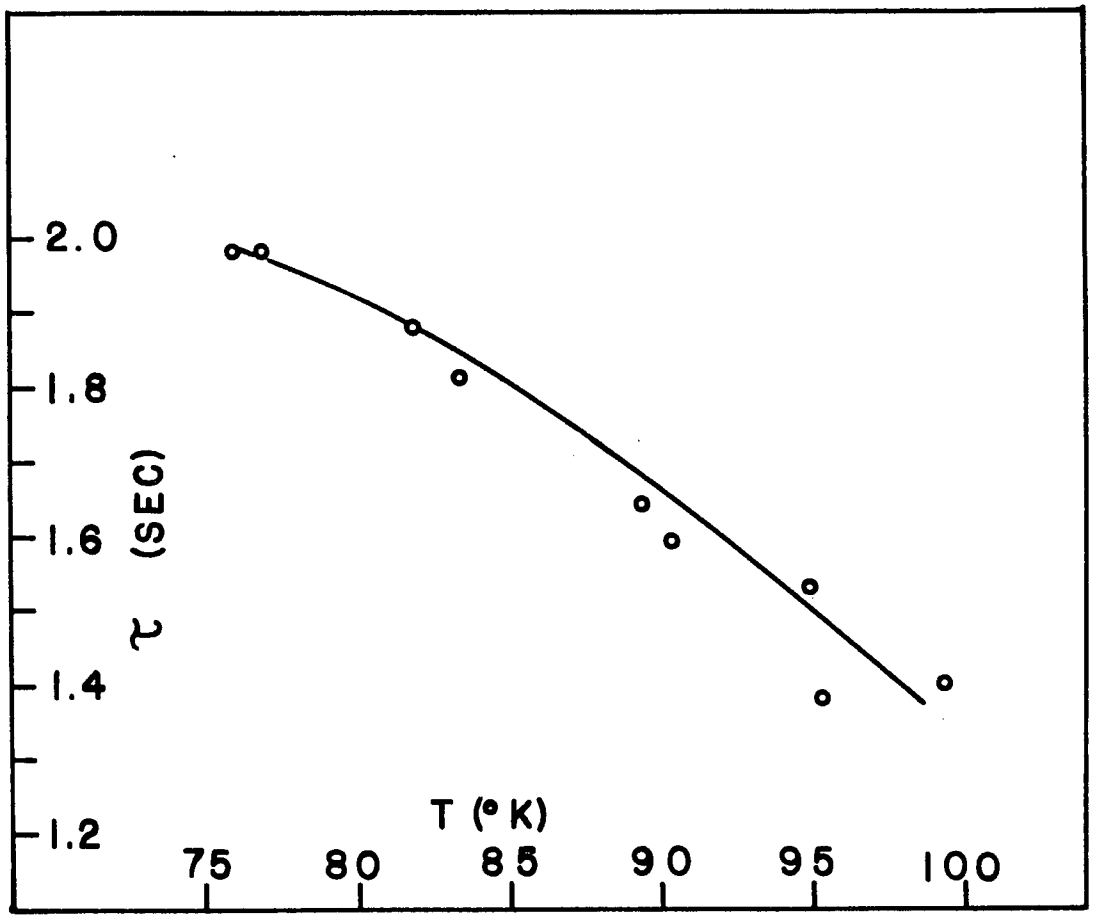

3.0
2.0
1.0
τ (SEC)
95
135
175
215
255
295
T (°K)

FIGURE 29. Mixed crystal system: chrysene in phenanthrene. Graph of lifetime versus temperature.


2.0
1.8
1.6
1.4
1.2
τ (SEC)
T (°K)
75
80
85
90
95
100

yield a straight line the slope of which is $-\Delta E/k$. This is shown in Figure 23. This was done for all systems which showed a sharp downturn in the curve of τ versus T. The temperature at which this downturn occurred is termed T_τ. This occurred in all the systems in which biphenyl was used as a host material. The results are seen in Table IV. In these systems the activation of $T_{IG} \rightarrow T_{IH}$ occurred at lower temperatures because of the smaller intermolecular energy gap. For the durene host systems $\Delta E(T_{IG} \rightarrow T_{IH})$ is large and the temperature of the downturn of the phosphorescence lifetime, T_τ, is not seen, but rather a steady increase in the rate of decline of lifetime with temperature. In Figures 30 through 38, graphs of the intensities of phosphorescence and delayed fluorescence as a function of temperature are presented. The temperature at which the downturn of the phosphorescence intensity occurs is denoted by T_{Ip} and the temperature at which the maximum of delayed fluorescence intensity occurs is denoted by T_{maxDF}. It is seen in Figure 39 that T_τ, T_{Ip} and T_{maxDF} increase linearly with the intermolecular energy difference. The equation of the line is T_τ, T_{Ip}, $T_{maxDF} \cong 0.06\ \Delta E(T_{IG} \rightarrow T_{IH})$.

A comparison of τ versus T behavior for the systems which yielded good results is shown in Figure 40. The curve labeled 1 shows the lifetime behavior of τ versus T for naphthalene-d_8 in durene. This is a guest molecule with a long lifetime. The system has a large $\Delta E(T_{IG} \rightarrow T_{IH})$ and it is seen that the downturn occurs at about 180° K. The curve labeled 2 is naphthalene-h_8 in durene; this system has the same ΔE $(T_{IG} \rightarrow T_{IH})$. Naphthalene-$h_8$ has a shorter phosphorescence lifetime, but qualitatively the two curves are alike.

TABLE IV

LUMINESCENCE DATA FOR VARIOUS MIXED CRYSTAL SYSTEMS

GUEST	$\Delta E_{therm.}$ (cm^{-1})	$\Delta E^{a}_{spect.}$ (cm^{-1})	T_{τ} (^{o}K)	T_{Ip} (^{o}K)	T_{maxDF} (^{o}K)
Phenanthrene Host:					
Chrysene	1200	1280	82	c	c
Biphenyl Host:					
Phenanthrene-d_{10}	1270	1610	95	100	125
Phenanthrene-h_{10}	1400	1630	115	105	135
Naphthalene-d_8	1790	1830	115	110	140
Naphthalene-h_8	2030	1940	110	125	150
Chrysene	2980	3350	185	185	220
Durene Host:					
Phenanthrene-d_{10}	4630	~3300	190	190	no DF
Phenanthrene-h_{10}	2920	3300	e	190	no DF
Naphthalene-d_8	3362[b]	3500	220[b]	e	no DF
Naphthalene-h_8	3558[b]	3610	240[b]	240	no DF
Chrysene	c	5000	e	e	110[d], 175[d]

a. These data are taken from T. N. Misra and S. P. McGlynn, J. Chem. Phys., 44, 3816 (1966).

b. These data are taken from S. G. Hadley, A. E. Rast, Jr., and R. A. Keller, J. Chem. Phys., 39, 705 (1963).

c. These numbers were not determinable with sufficient accuracy.

d. Impurity interference is evident in this instance.

e. No well-defined characteristic temperatures were observed.

FIGURE 30. Mixed crystal system: phenanthrene in biphenyl. Graph of relative intensity of phosphorescence and fluorescence *versus* temperature.

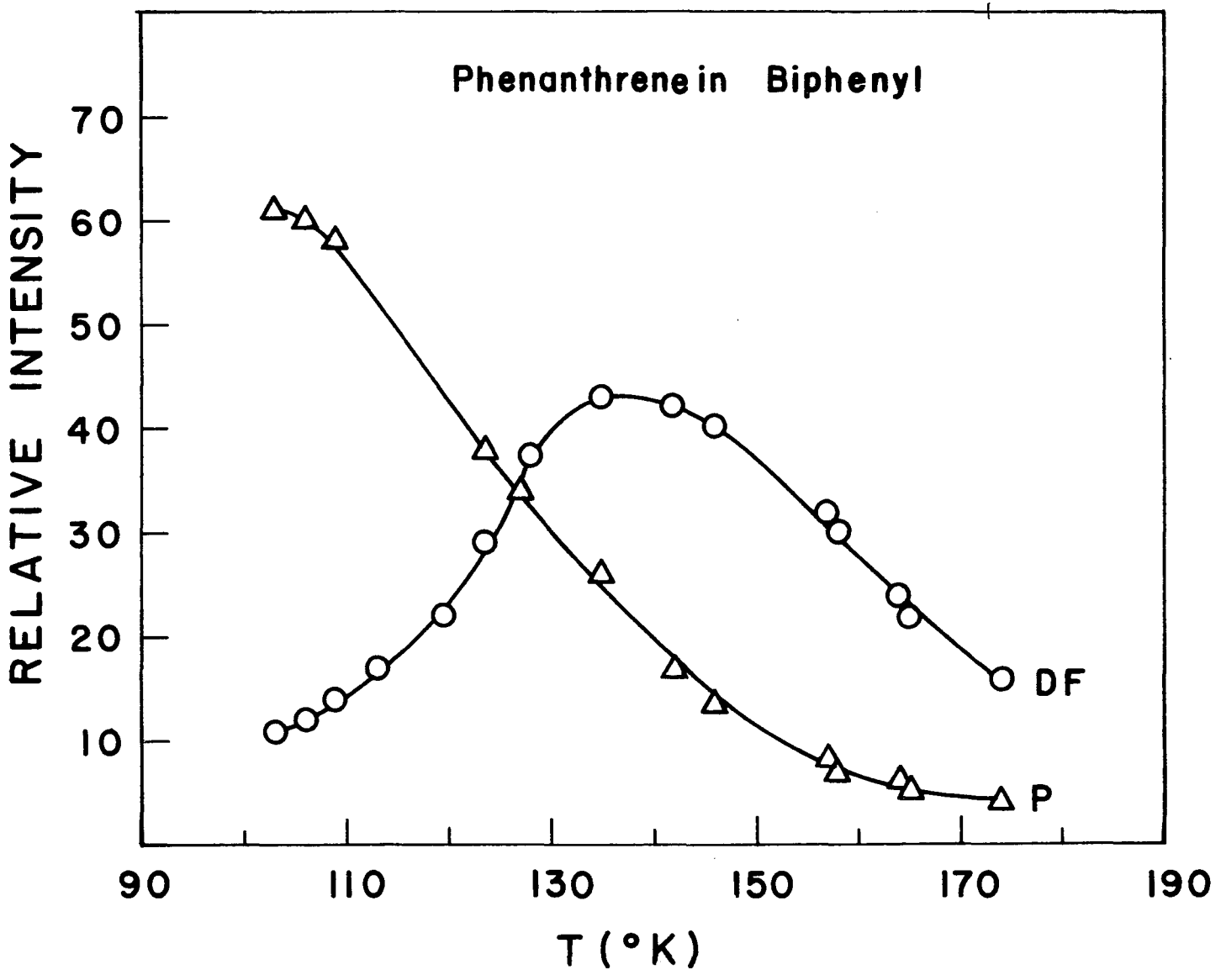

Phenanthrene in Biphenyl
RELATIVE INTENSITY
70
60
50
40
30
20
10
90
110
130
150
170
190
T (°K)
DF
P

FIGURE 31. Mixed crystal system: phenanthrene-d_{10} in biphenyl. Graph of relative intensity of phosphorescence and fluorescence *versus* temperature.

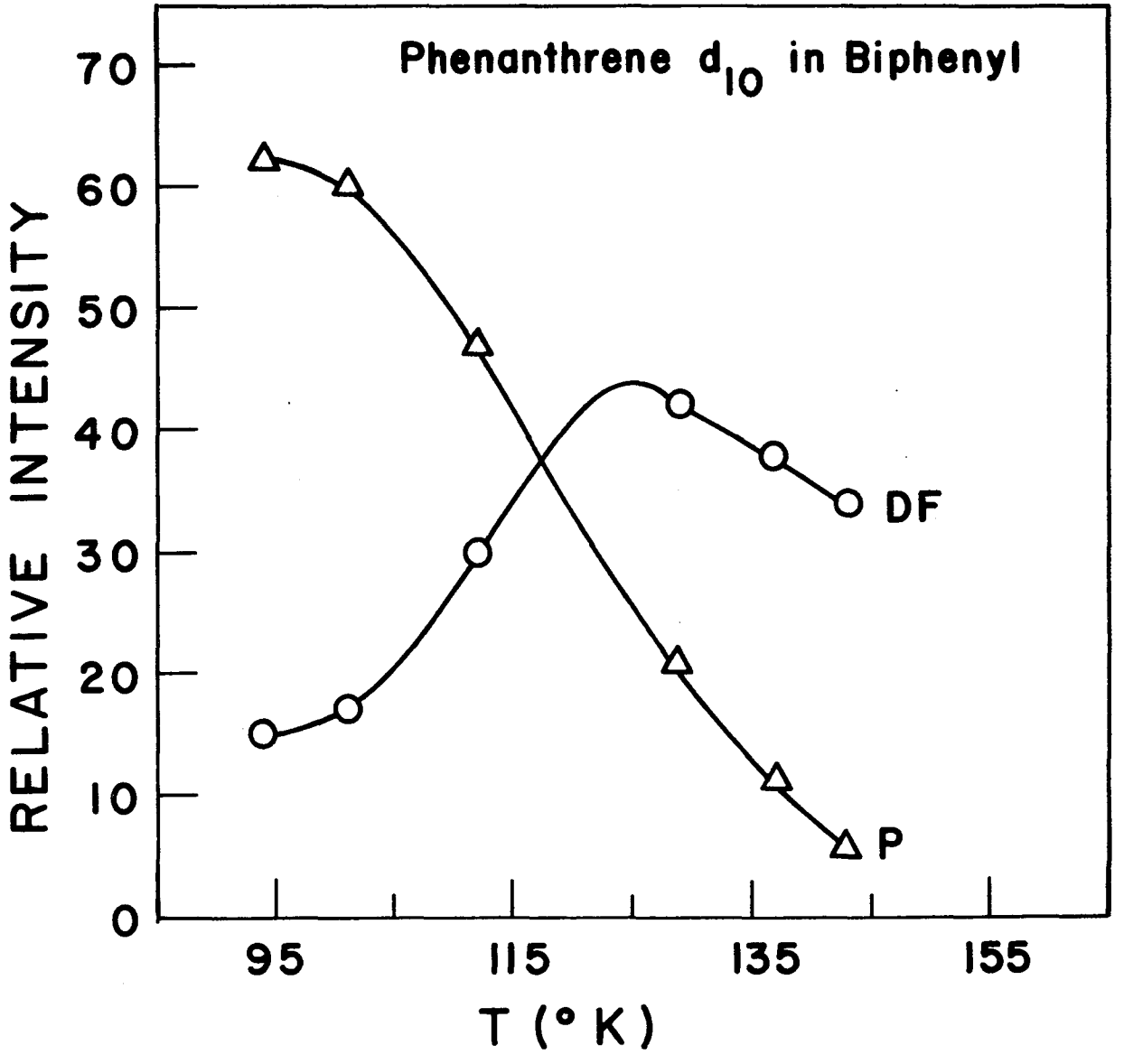

Phenanthrene d_{10} in Biphenyl
RELATIVE INTENSITY
70
60
50
40
30
20
10
0
95
115
135
155
T (° K)
DF
P

FIGURE 32. Mixed crystal system: chrysene in biphenyl. Graph of relative intensity of phosphorescence and fluorescence *versus* temperature.

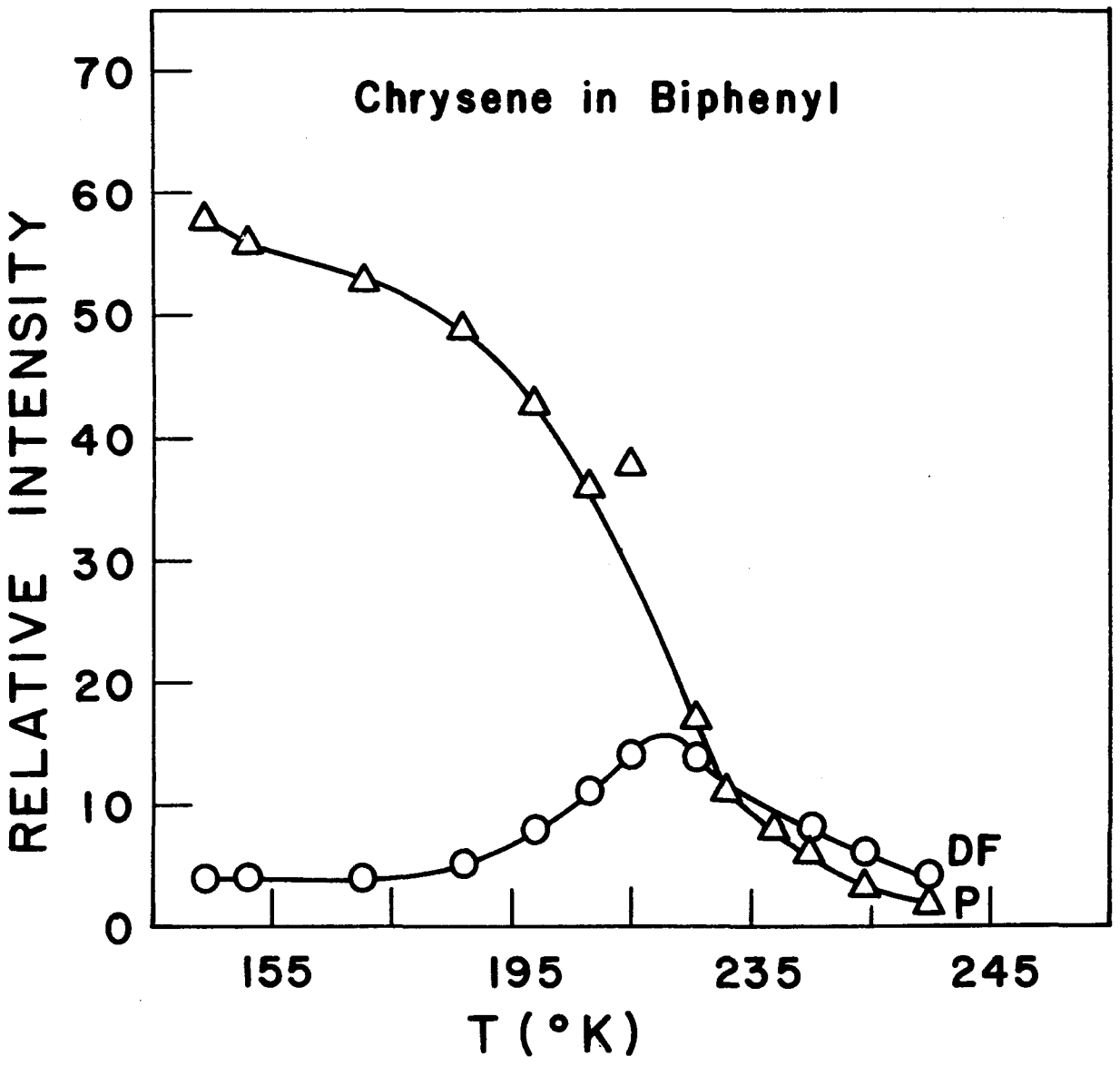

Chrysene in Biphenyl
RELATIVE INTENSITY
70
60
50
40
30
20
10
0
155
195
235
245
T (°K)
DF
P

FIGURE 33. Mixed crystal system: naphthalene-d_8 in biphenyl. Graph of relative intensity of phosphorescence and fulorescence *versus* temperature.

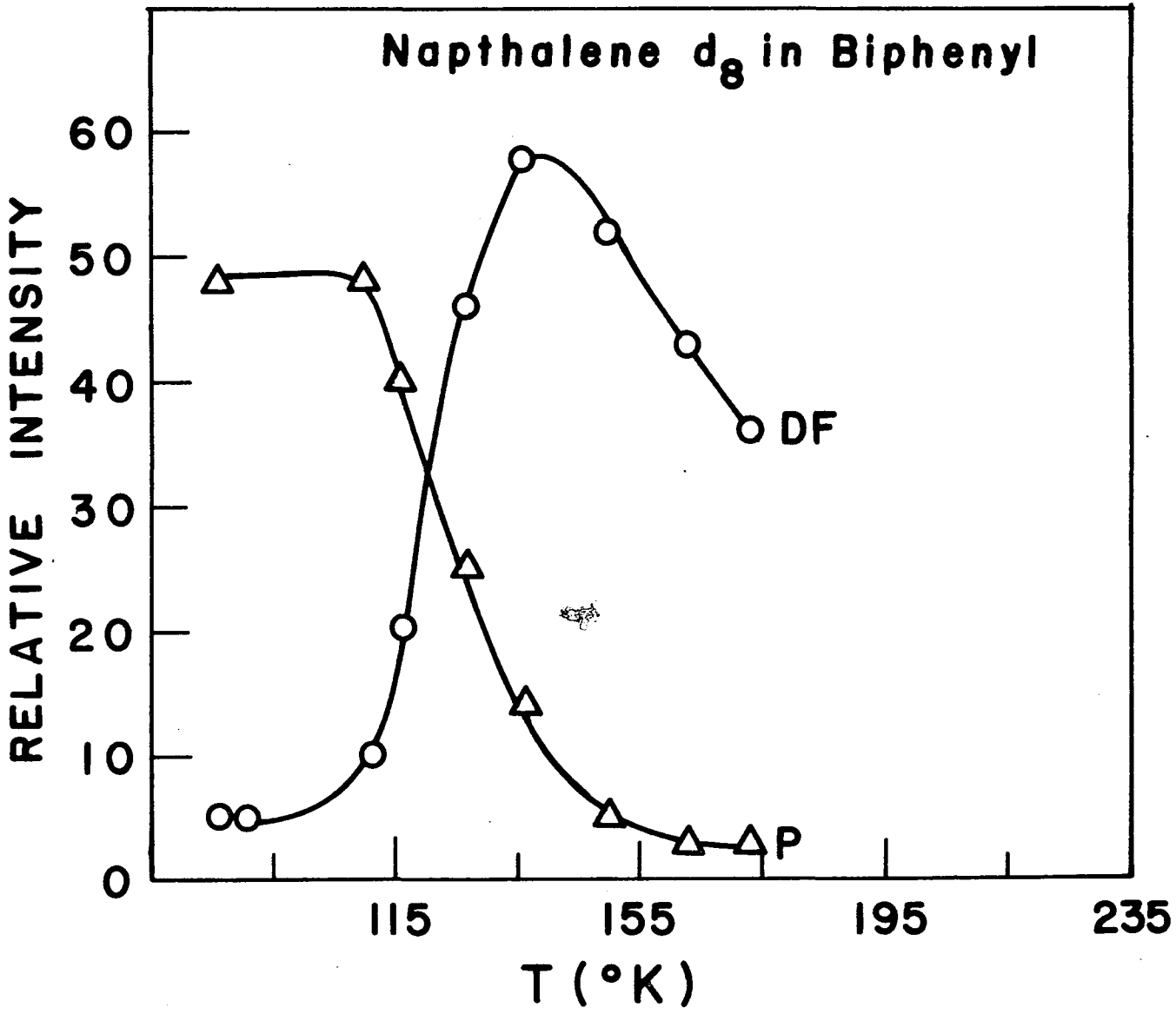

Napthalene d_8 in Biphenyl
RELATIVE INTENSITY
60
50
40
30
20
10
0
DF
P
115
155
195
235
T (°K)

FIGURE 34. Mixed crystal system: naphthalene in biphenyl. Graph of relative intensity of phosphorescence and fluorescence *versus* temperature.

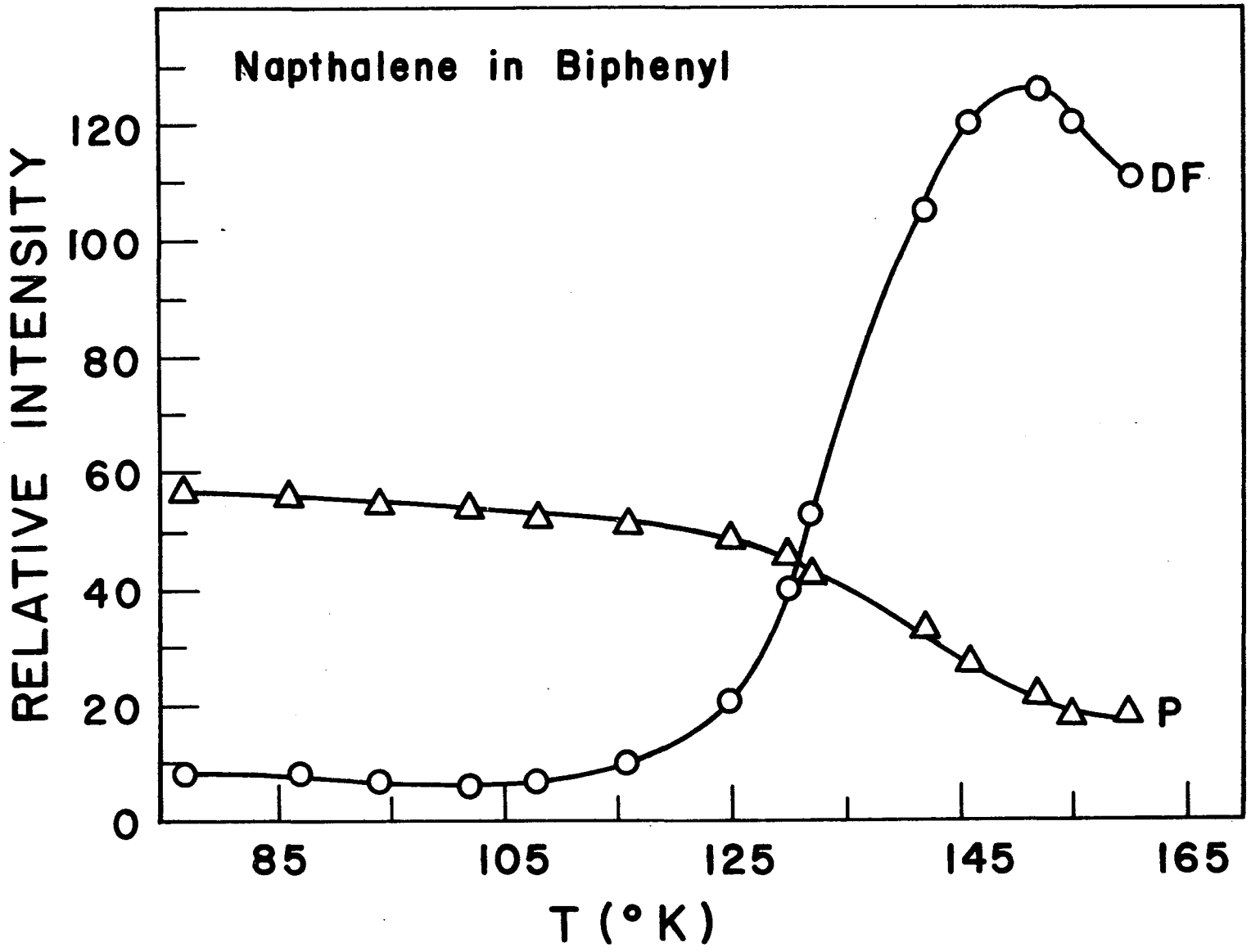

Napthalene in Biphenyl
RELATIVE INTENSITY
120
100
80
60
40
20
0
85
105
125
145
165
T (°K)
DF
P

FIGURE 35. Mixed crystal system: phenanthrene in durene. Graph of relative intensity of phosphorescence versus temperature.

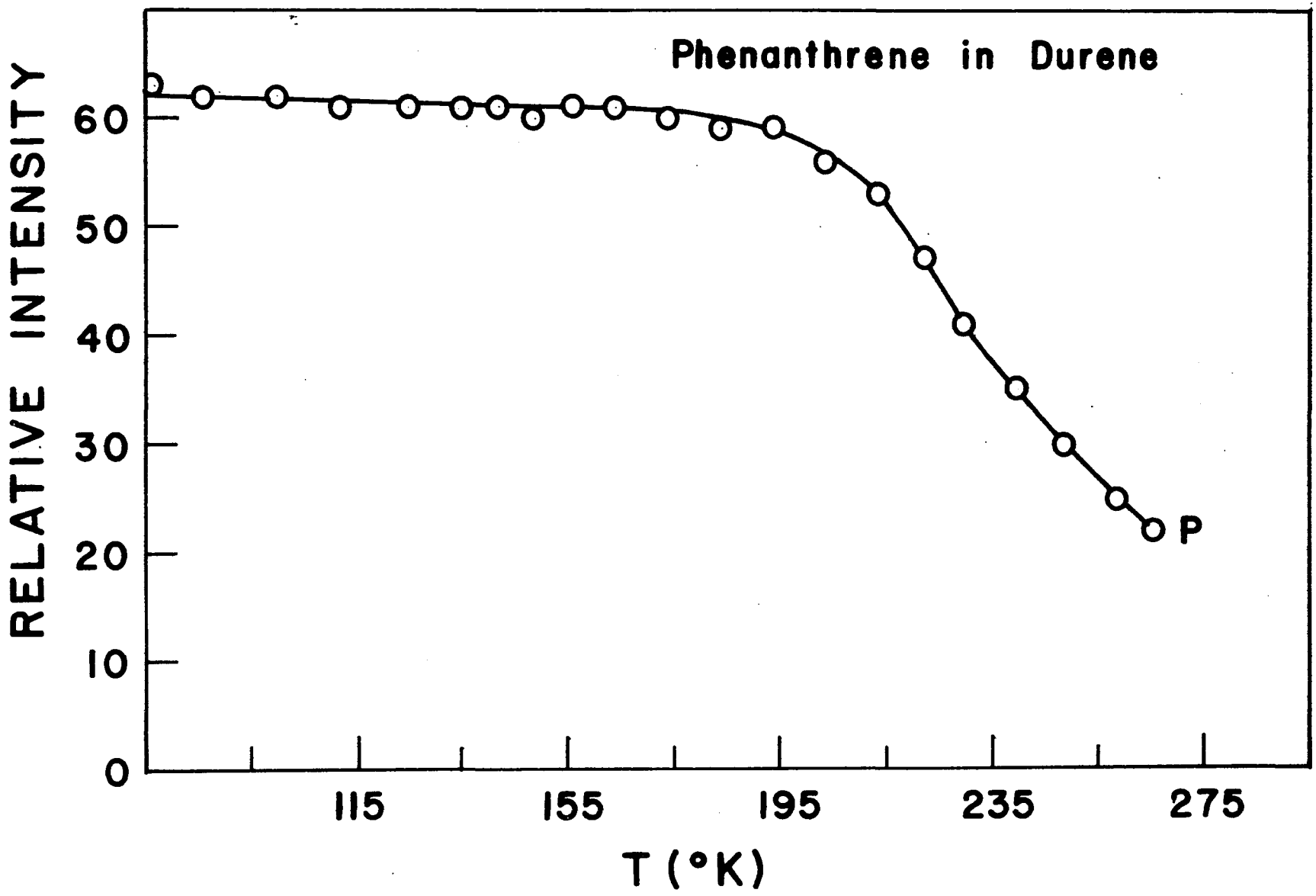

Phenanthrene in Durene
RELATIVE INTENSITY
60
50
40
30
20
10
0
115
155
195
235
275
T (°K)
P

FIGURE 36. Mixed crystal system: chrysene in durene. Graph of relative intensity versus temperature. Delayed fluorescence (open circles), phosphorescence (filled circles).

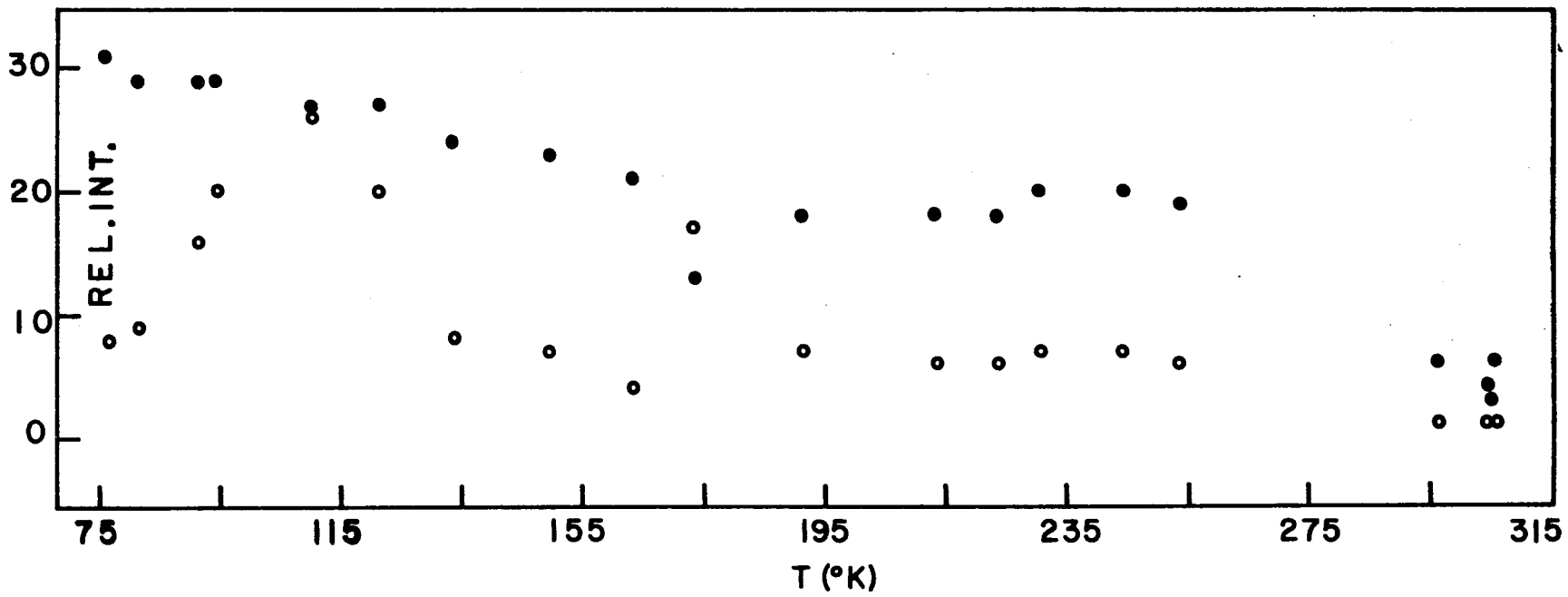

30
20
10
0
REL. INT.
75
115
155
195
235
275
315
T (°K)

FIGURE 37. Mixed crystal system: naphthalene in durene. Graph of relative intensity of phosphorescence versus temperature.

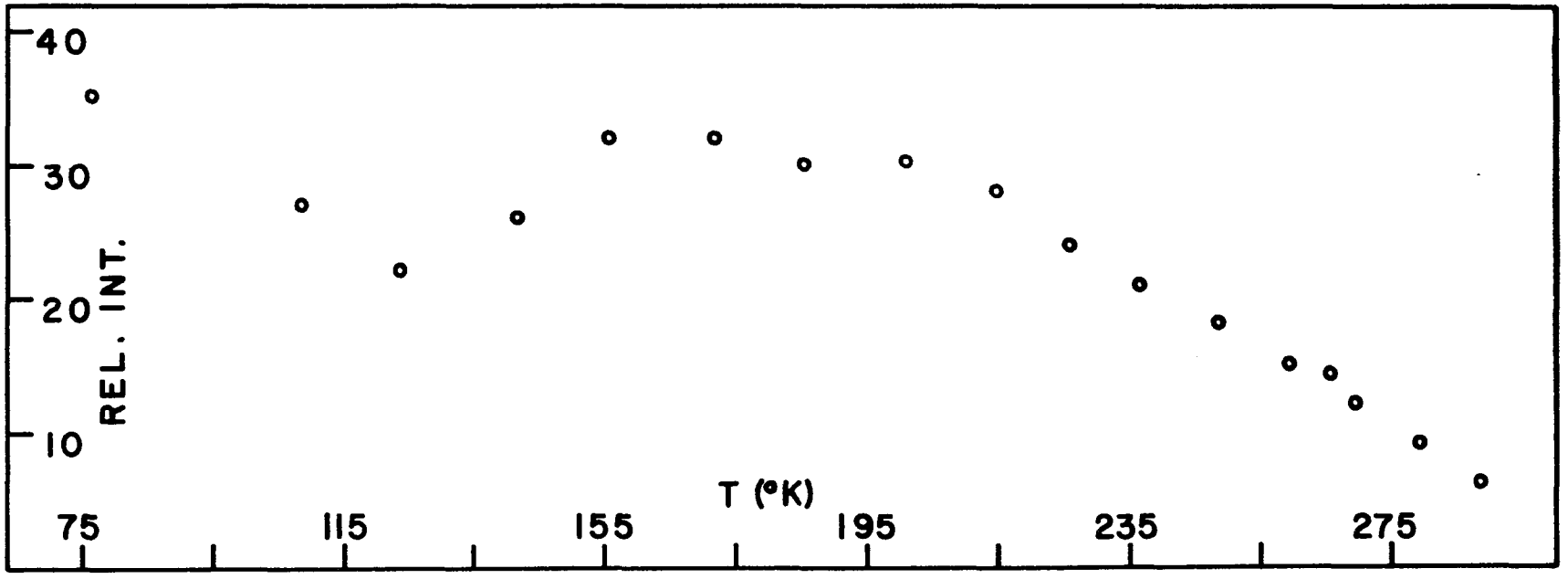

40
30
20
10
REL. INT.
T (°K)
75
115
155
195
235
275

FIGURE 38. Mixed crystal system: naphthalene in durene. Graph of relative intensity of phosphorescence versus temperature.

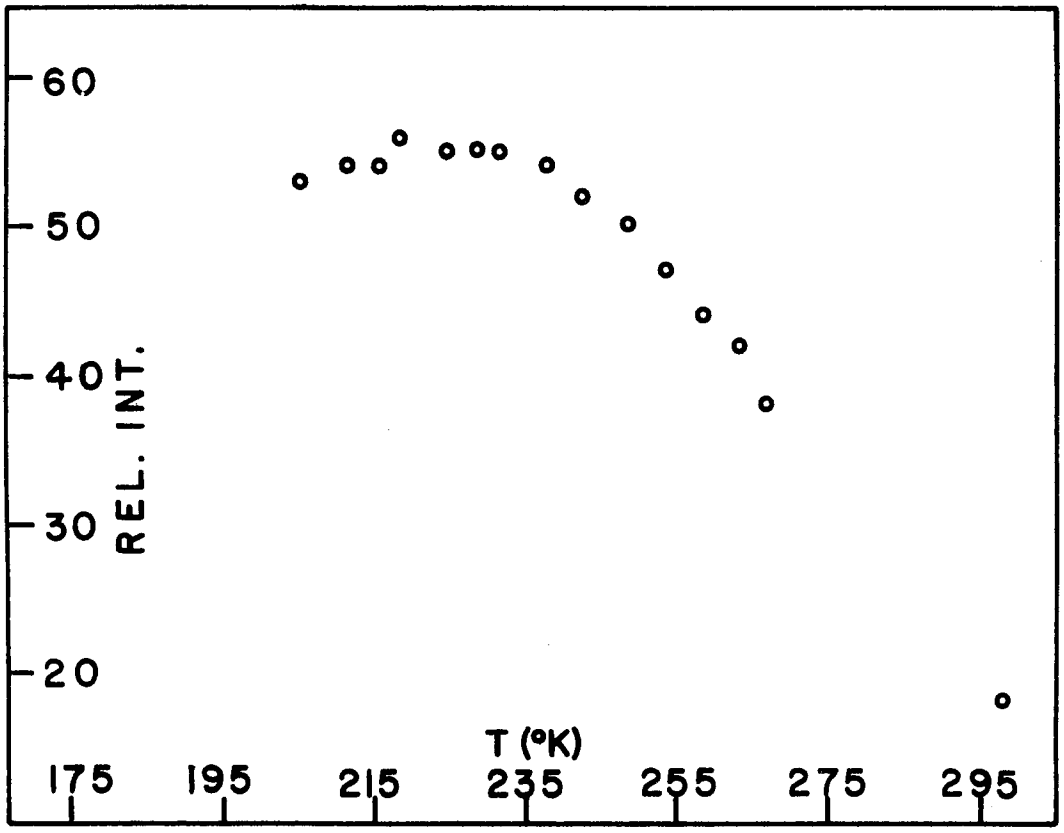

60
50
40
30
20
REL. INT.
T (°K)
175
195
215
235
255
275
295

FIGURE 39. Plots of characteristic temperatures, T_{TP}, T_{Ip} and T_{maxDF} <u>versus</u> $\Delta E(T_{IH} \rightarrow T_{IG})$.

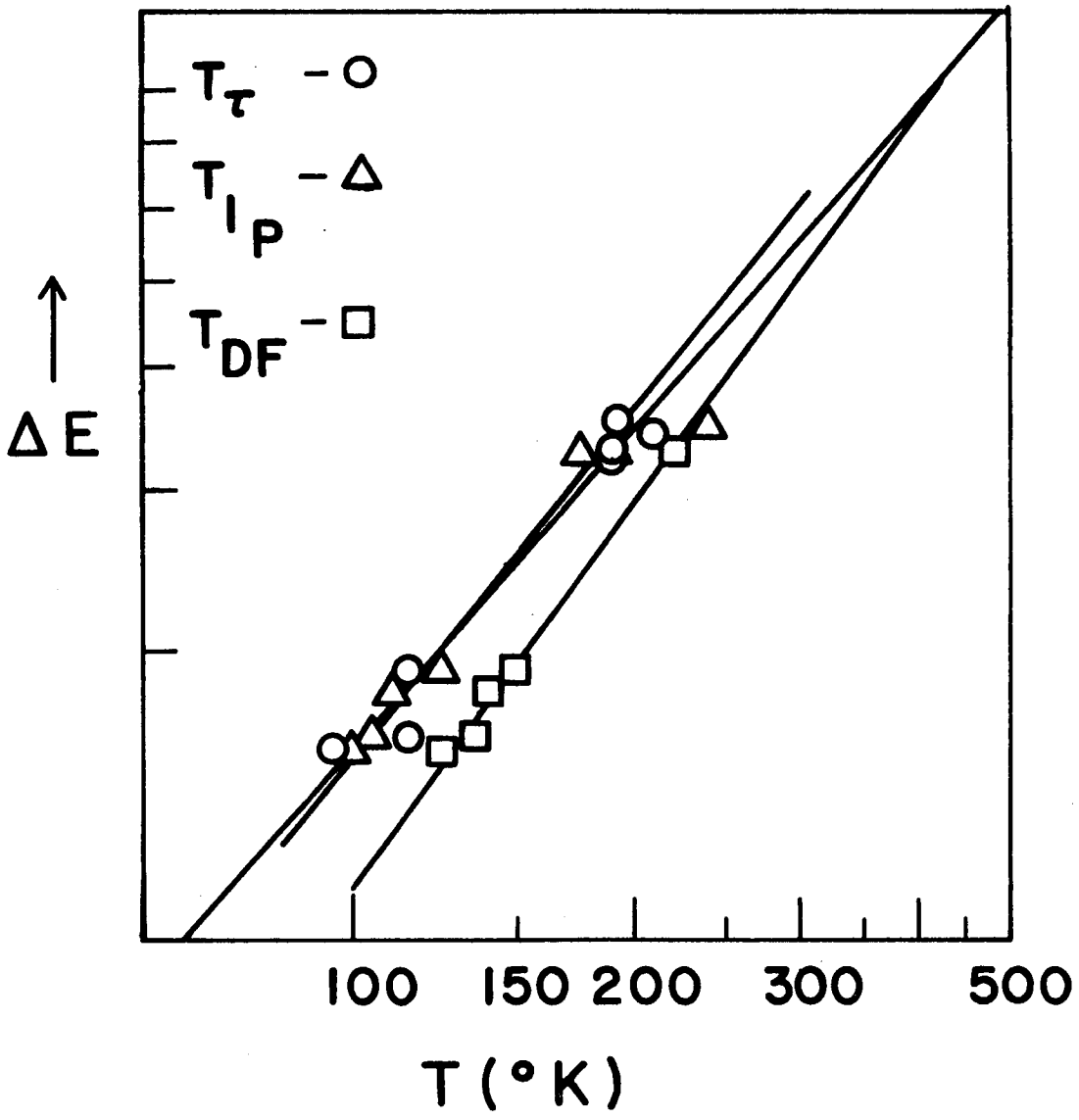

T_τ - O
T_{I_P} - Δ
T_{DF} - □
ΔE
100
150
200
300
500
T (°K)

FIGURE 40. Lifetime *versus* temperature behavior for seven systems:

1. Naphthalene-d_8 in durene.
2. Naphthalene-h_8 in durene.
3. Naphthalene-d_8 in biphenyl.
4. Naphthalene-h_8 in biphenyl.
5. Phenanthrene-h_{10} in durene.
6. Phenanthrene-d_{10} in biphenyl.
7. Phenanthrene-h_{10} in biphenyl.

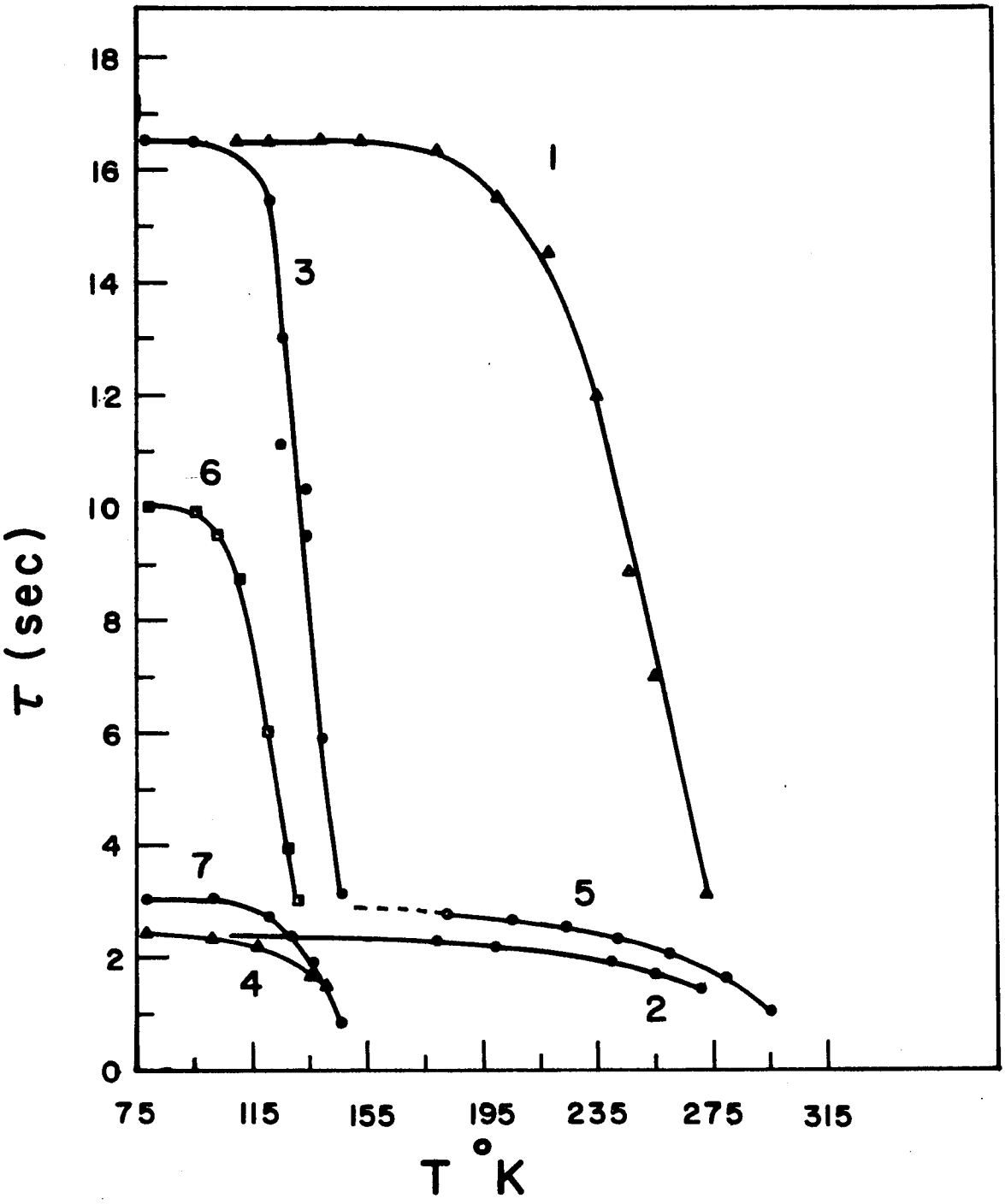

18
16
14
12
10
8
6
4
2
0
τ (sec)
75
115
155
195
235
275
315
T °K
1
2
3
4
5
6
7

Figure 40 shows curves labeled 3 and 4 which represent the behavior of perdeuterated and protonated naphthalene in biphenyl, respectively. These curves are qualitatively alike in their temperature dependence behavior. The curve labeled 5 shows the lifetime behavior of phenanthrene-h_{10} in durene. Here $\Delta E(T_{IG} \rightarrow T_{IH})$ is large; consequently, the system does not yield this energy difference due to some interference effects to be mentioned later.

Figure 41 shows the temperature dependence of a single guest in three different host materials. The behavior of the lifetime versus temperature is shown for chrysene in (1) phenanthrene-h_{10}, (2) biphenyl, and (3) durene. These curves emphasize the importance of $\Delta E(T_{IG} \rightarrow T_{IH})$ to the radiationless process of thermal activation.

Figure 42 shows the Arrhenius plots of log $(\frac{1}{\tau} - \frac{1}{\tau_O})$ versus $\frac{1}{T}$ for different systems. Curves 1 and 2 show phenanthrene-d_{10} and phenanthrene-h_{10} in durene, respectively. Curve 3 shows chrysene in biphenyl and 4 shows chrysene in phenanthrene-h_{10}. The two phenanthrenes in durene show the same activation energies: their graphs are parallel; however, chrysene in two different host materials shows lines of different slopes, indicating different activation energies. Curves 5 and 6 are naphthalene-d_8 and naphthalene-h_8 in biphenyl. The energies are again alike, for the slopes of the Arrhenius plots are equal. This is also true of 7 and 8, phenanthrene-d_{10} and phenanthrene-h_{10} in biphenyl, respectively.

A graph of relative intensity versus temperature for two different systems is presented in Figure 43 to illustrate in another aspect the role of $\Delta E(T_{IG} \rightarrow T_{IG})$ on triplet-triplet annihilation. Here the two systems employ biphenyl as the host with different guests,

FIGURE 41. Lifetime versus temperature for chrysene in (1) phenanthrene-h_{10}, (2) biphenyl, (3) durene.

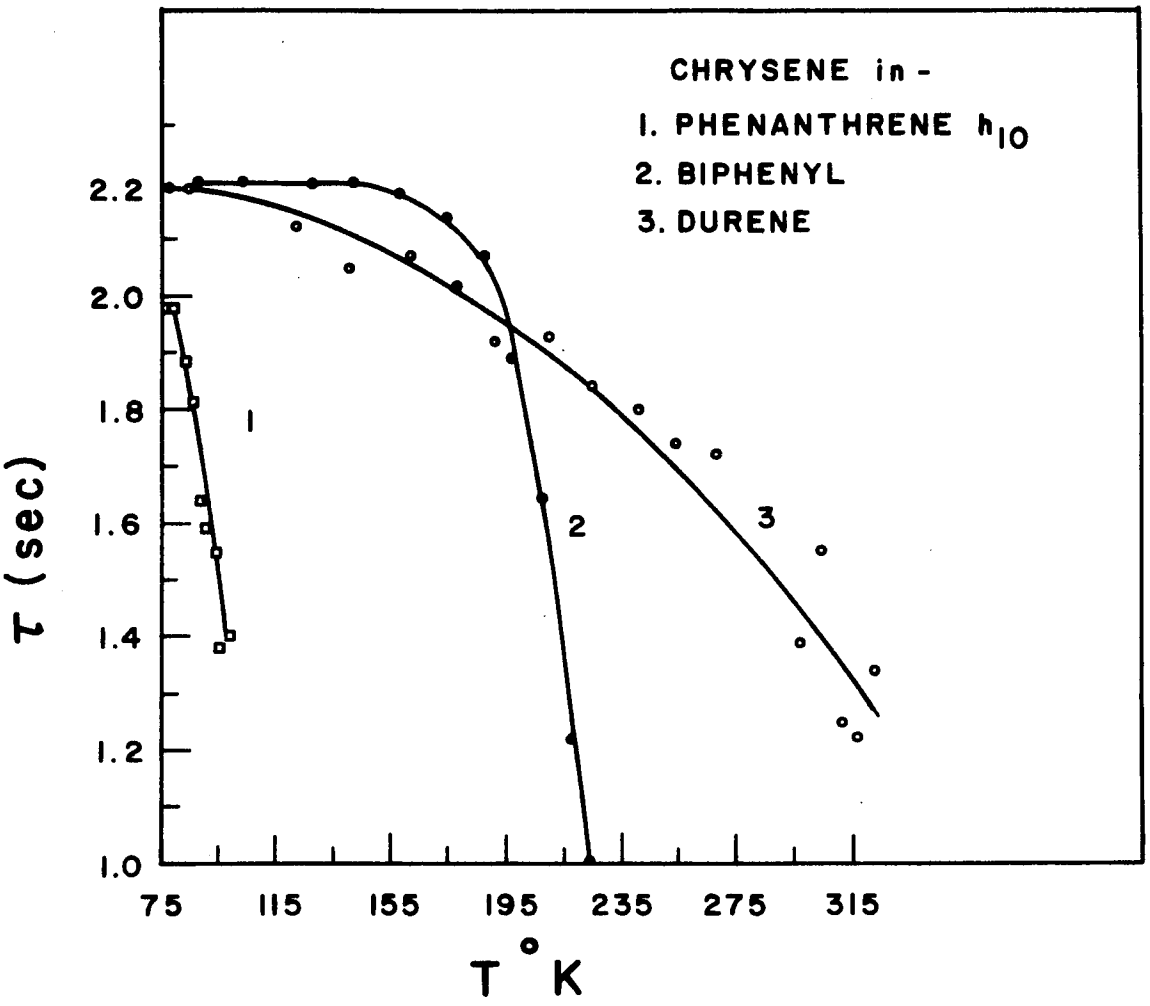

CHRYSENE in -
1. PHENANTHRENE h_{10}
2. BIPHENYL
3. DURENE
τ (sec)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
1
2
3
75
115
155
195
235
275
315
T °K

FIGURE 42. Log $(\frac{1}{\tau} - \frac{1}{\tau_0})$ versus $\frac{1}{T}$ for eight systems:

1. Phenanthrene-d_{10} in durene.
2. Phenanthrene-h_{10} in durene.
3. Chrysene in biphenyl.
4. Phenanthrene-h_{10} in biphenyl.
5. Naphthalene-d_8 in biphenyl.
6. Naphthalene-h_8 in biphenyl.
7. Phenanthrene-d_{10} in biphenyl.
8. Chrysene in phenanthrene-h_{10}

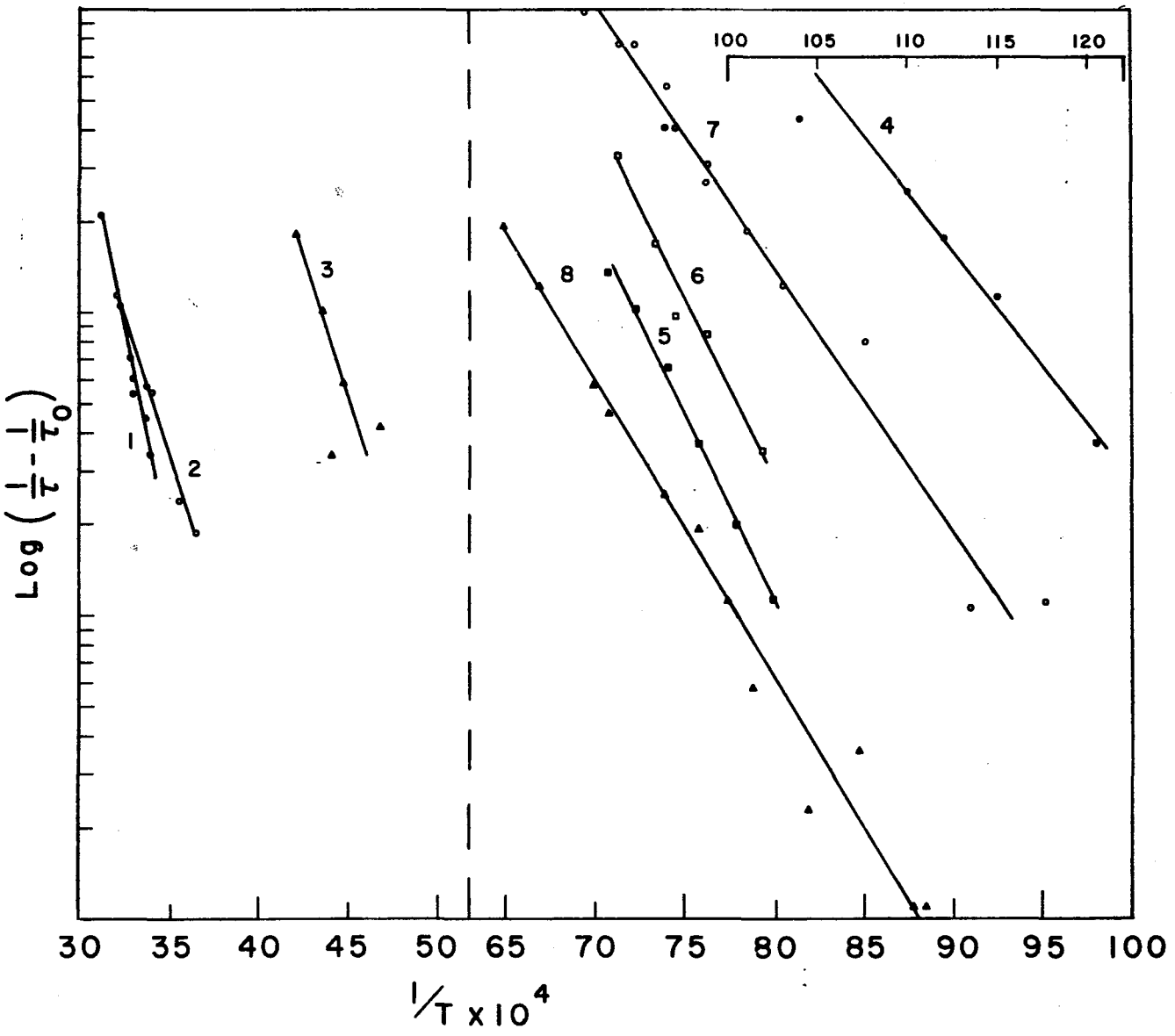
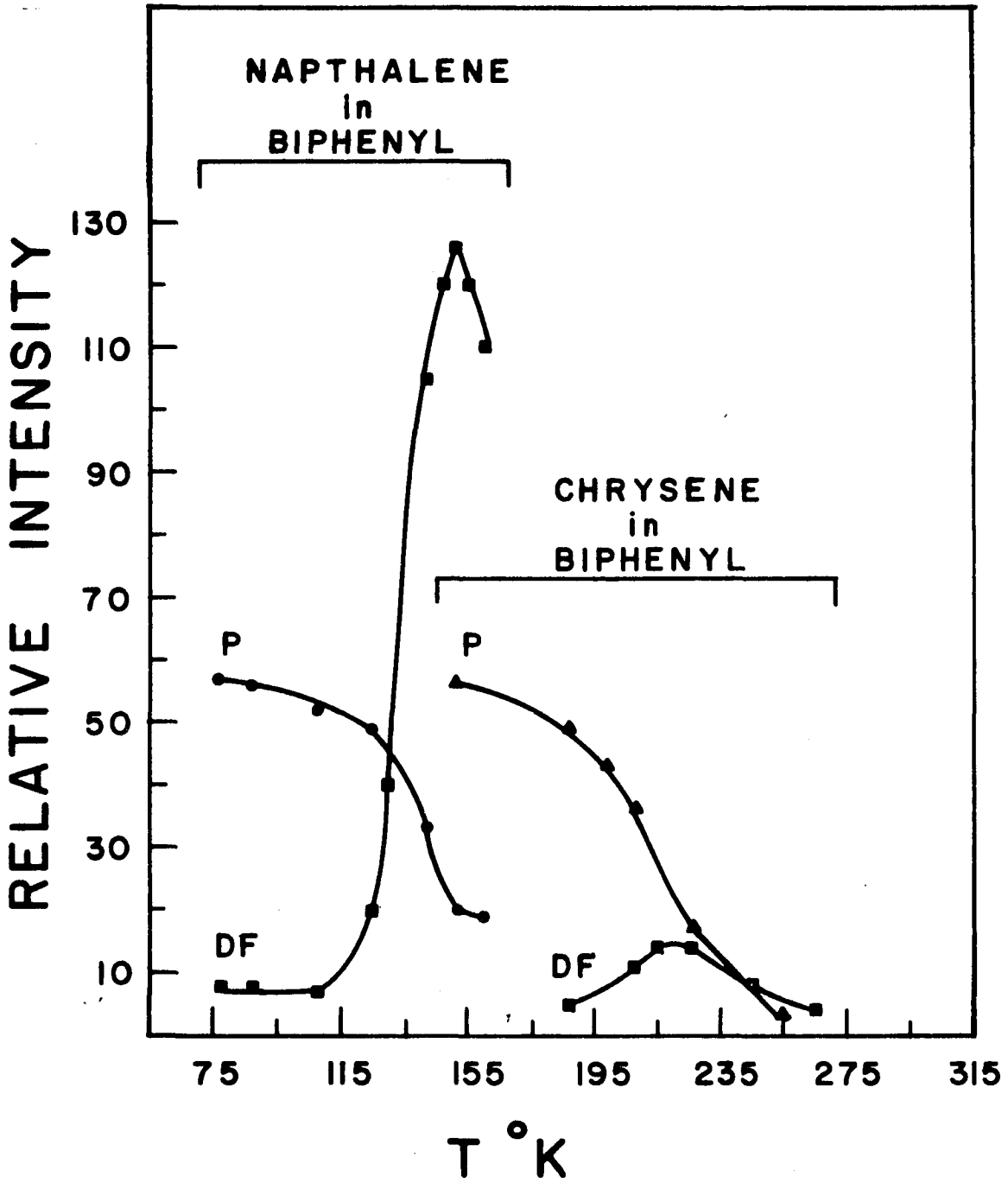

100
105
110
115
120
1
2
3
4
5
6
7
8
$\log\left(\frac{1}{\tau}-\frac{1}{\tau_0}\right)$
30
35
40
45
50
65
70
75
80
85
90
95
100
$1/T \times 10^4$

FIGURE 43. Comparison of relative intensities of two systems as a function of temperature.


NAPTHALENE
in
BIPHENYL
CHRYSENE
in
BIPHENYL
P
P
DF
DF
RELATIVE INTENSITY
130
110
90
70
50
30
10
75
115
155
195
235
275
315
T °K

naphthalene-h_8 and chrysene; the naphthalene-h_8 in biphenyl system has a smaller energy gap, $\Delta E(T_{IG} \rightarrow T_{IH})$, than has chrysene in biphenyl. The former system has 1940 cm^{-1} (spectroscopic) while the latter has 5000 cm^{-1} (spectroscopic). It is observed that T_{Ip} and T_{maxDF} occur at higher temperatures for the latter than for the former system. This is regarded as further evidence of the radiationless thermal activation process.

Table IV shows that the results of the experimental work are in good agreement with the spectroscopic energy difference for the phenanthrene and biphenyl host systems confirming the intermolecular radiationless process $T_{IG} \rightarrow T_{IH}$. The durene data which is not in good agreement is presented. Little effort was expended on durene systems for the following reasons: durene is easily decomposed to produce the duryl radical; durene has the largest value for $E(T_1)$ and for large energy gaps between host and guest triplet states much of the annihilative process is interfered with by impurities or defects which have triplet states between $E(T_{IG})$ and $E(T_{IH})$.

4. Conclusions

Upon reviewing the results from the experimental data in Figures 39, 40, 41, 42, and 43, the conclusion must be drawn that the matrix (i.e., host of the mixed crystal system) has a very central role in the behavior of lifetime and intensity of both phosphorescence and delayed fluorescence. This central role manifests itself by providing the upper energy level to which energy trapped in the guest triplet level (Figure 22) is activated thermally. When the thermal activation has been accomplished, delayed fluorescence intensity increases with a

corresponding decrease in phosphorescence intensity. It is seen that this model and these assumptions about radiationless transitions and about process types (intra- and intermolecular) have been experimentally shown to be correct. Table IV shows that $\Delta E(T_{IG} \rightarrow T_{IH})$ has been found by thermal activation and can be related to the spectroscopically determined energy difference which leaves no doubt as to the intermolecular thermal activation process. Supporting evidence, if any be needed, is best shown by Figure 39, which plots the characteristic temperatures, T_{τ}, T_{Ip} and T_{maxDF} for each system versus the host-guest difference; a linear relationship is shown, further evidence of the intermolecular process.

CHAPTER III

LUMINESCING SOLUTES IN POLYMETHYLMETHACRYLATE

1. Introduction

An extension of the work on mixed crystal systems described in Chapter II is provided by the use of solid "solvents" other than organic crystals. Plastics readily lend themselves to employment in such temperature dependence studies: they can be made in transparent form and the plastic monomer readily dissolves an aromatic luminescent solute.

Kellogg and Schwenker[24] studied the temperature dependence of the phosphorescence of luminescing solutes in polymethylmethacrylate. They generated experimental plots of phosphorescence lifetime versus temperature for various aromatics in several different plastic media. They hoped to ascertain, by these studies, whether the theory of radiationless transitions given by Gouterman[3] was superior to that proposed by Robinson and Frosch.[1]

Our purpose, however, is to attempt to determine if effects like those present in mixed crystals are also operative in plastics. We wished to know if energy in the triplet state of the solute could be transferred by radiationless means to the triplet state of the plastic solvent. This, indeed, was the expected behavior. Due to the randomness of the structure of the plastic matrix, it was thought that the plastic solvent would not form exciton bands as do molecules of the host crystalline lattice. We expected that this energy, once in the plastic polymer chain, would be transferred within the chain for short distances; thereafter, we expected that this excitation energy would be transferred to a solute molecule other than the one which furnished the

original excitation to the polymer chain. It was even thought that some triplet-triplet annihilation might occur, particularly if the solute triplet to the plastic triplet energy differences were not too large and if the two solute molecules were not too far apart along the plastic chain. If the energy gap is too large, as is the case with chrysene in durene, no triplet-triplet annihilation would be expected to take place.

In order to carry out the experimental studies, polystyrene, polymethylmethacrylate, polyvinylacetate and polymethacrylonitrile were chosen as the plastic "solvents". The solutes chosen for dissolving in these "matrices" were phenanthrene-h_{10} and -d_{10}, biphenyl-h_{10} and -d_{10}, and durene. These choices result in twenty possible binary systems which have a range of $\Delta E[T_1(\text{solute}) - T_1(\text{solvent})]$ values between 5000 and 10,000 cm^{-1}.

2. Experimental

a) Method of obtaining plastic solvents

Methylmethacrylate, vinylacetate and methacrylonitrile were distilled using a column packed with glass beads. Distillation was carried out at a pressure of 600 mm Hg pressure in order to free the monomer of the stabilizer. Styrene was not distilled when it was learned that it would not polymerize to a solid as would methylmethacrylate. Styrene forms a viscous fluid from which may be isolated a white, fleecy solid which is a polymer of low molecular weight. To obtain high molecular weight polystyrene requires treatment too drastic to make it suitable for luminescence work.

b) Addition of initiator; degassing of monomer; polymerization

Methylmethacrylate, vinylacetate and acrylonitrile were used as trial solvents. The initiator for radical polymerization, azo-(bis)-isopropylcyanide (AIBN), was added to a concentration of 5×10^{-4} m/l. The tubes of monomer were then attached to a high vacuum system and degassed as follows: the tube of monomer was immersed in liquid nitrogen; when the monomer was solid the valve to the vacuum chamber was opened and the gas above was withdrawn. When a low vacuum was obtained ($\sim 10^{-4}$ mm Hg) the valve to the vacuum chamber was closed and the solid monomer was allowed to thaw. This freeze-thaw cycle was repeated three times, after which it was considered that the monomer was sufficiently well deoxygenated. The tubes were then sealed and placed in a well-regulated oven at 60° C. After two and one-half days the methylmethacrylate was polymerized. This monomer was then considered usable as a solvent for the solutes mentioned above. Methacrylonitrile and vinylacetate did not polymerize when treated in the same manner as the methylmethacrylate. Repeated trials to polymerize these monomers were fruitless and they were dropped from consideration as forming convenient plastic matrices. Polystyrene was obtained in a pure form as a low molecular weight solid and dissolved in benzene; a luminescing solute was added. This was poured onto a quartz plate and the solvent was allowed to evaporate at a slightly elevated temperature. When the emission spectrum of this specimen was observed, it was seen to consist of a broad, structureless band characteristic of polystyrene. The solute luminescence was not seen. For this reason, polystyrene as a "solvent" also had to be eliminated from these studies.

When it was apparent that only polymethylmethacrylate could be used as a plastic matrix, we decided to delete durene from the possible solutes and compare the effects of deuteration on the phosphorescence behavior with temperature using four different solutes: phenanthrene-h_{10} and -d_{10}, and biphenyl-h_{10} and -d_{10}.

c) Temperature measurement and control

The measuring and temperature control apparatus used here was the same as that used in studies on mixed crystals.

d) Preparation of the plastic solution for measurement

After polymerization was complete, the samples were removed from the tubes; flat faces were cut into the cylinders of the plastic matrix so that the solute could be properly irradiated and a maximum intensity of the emitted light could be obtained at the analyzing optics.

3. Results and discussion

a) Stability of polymethylmethacrylate as a "solvent"

In our experiments with polymethylmethacrylate as a matrix for luminescing solutes it was found that the "solution" did not differ from specimen to specimen. Standing over a two-month period also did not affect the emission spectrum in any way. Reproducibility of this type of system seems to present no difficulty whatever. The radical initiator, AIBN, did not interfere with measurements, for it neither showed any luminescence, nor did it have any effect on the solute luminescence.

b) Comparison of graphs of deuterated and protonated biphenyl and phenanthrene

Graphs depicting the behavior of lifetimes *versus* temperature are presented for four solutes in polymethylmethacrylate: biphenyl-h_{10}, biphenyl-d_{10}, phenanthrene-h_{10} and phenanthrene-d_{10}; the graphs are labeled Figures 44 through 47, respectively. So that comparison may be made easier, graphs of τ/τ_{max} as a function of temperature for the two biphenyls and for the two phenanthrenes have been made; these are Figures 48 and 49, respectively. Inspection of these two figures shows that the behavior of the lifetimes of phosphorescence as a function of temperature for the two perdeuterated solutes is opposite in effect. The lifetime of biphenyl-d_{10} has a faster rate of decrease with temperature than has its protonated counterpart while that of phenanthrene-d_{10} has a slower rate of decrease than its perprotonated counterpart.

Of some interest is the observation that the lifetime of phenanthrene-d_{10} in the plastic appears to be asymptotically approaching some limiting value near 10.5 seconds as the temperature is raised.

The manner in which the lifetimes of the protonated solutes appear to decrease in a step-wise fashion with temperature is very curious, indeed. This effect is not nearly so pronounced in the perdeuterated solutes.

There seems to be no apparent reason why the protonated and deuterated solutes of biphenyl and phenanthrene should exhibit such contrary behavior as they do. The stepwise decrease of lifetime *versus* temperature of protonated solutes is probably a property of the plastic matrix and not of the solute. If this is true, its appearance only with protonated solutes is fortuitous.

The difference in the rates of decay of phosphorescence of deuterated and protonated solutes with temperature is probably due to

FIGURE 44. Lifetime versus temperature for biphenyl-h_{10} in lucite.

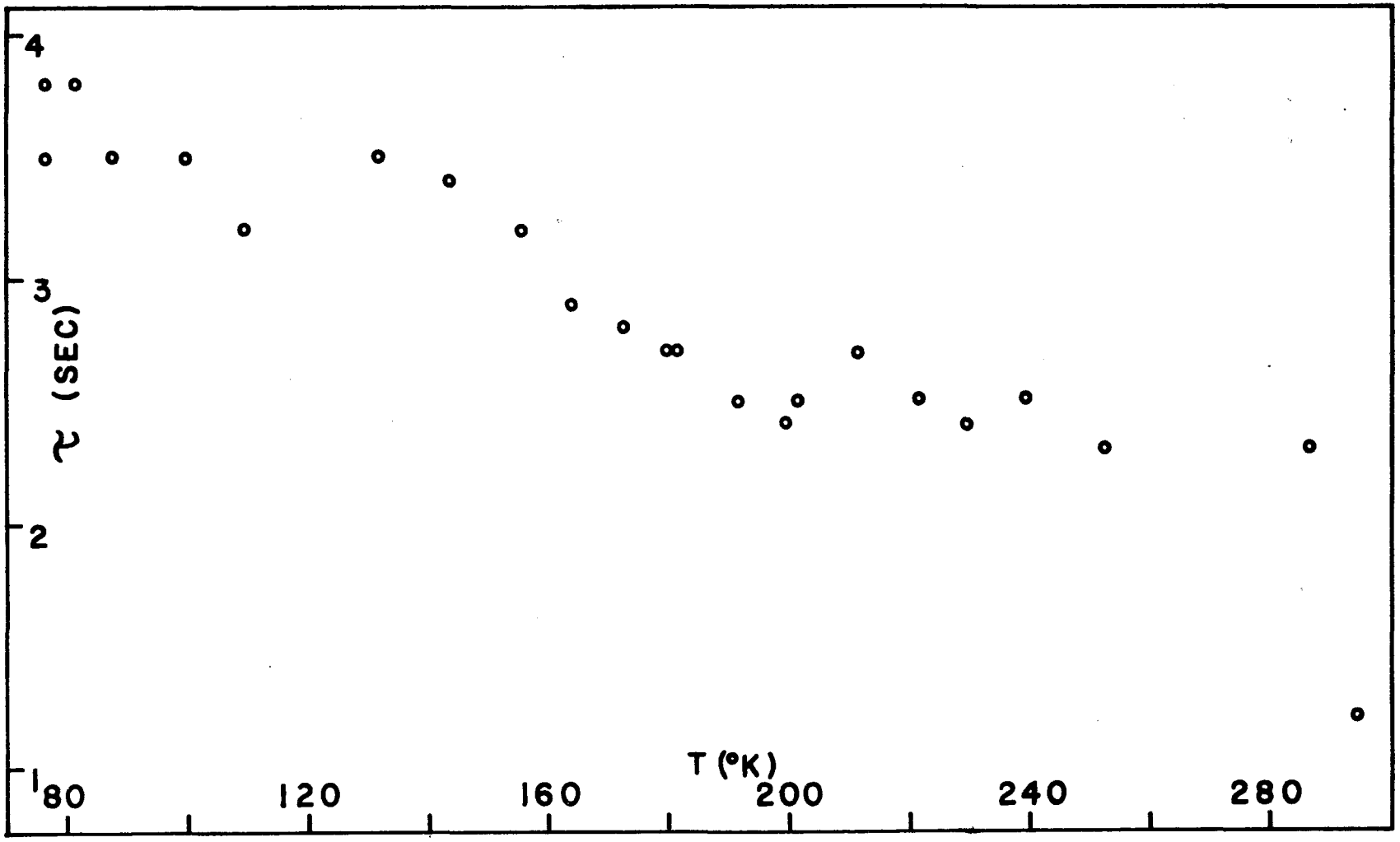

4
3
2
1
τ (SEC)
80
120
160
200
240
280
T (°K)

FIGURE 45. Lifetime versus temperature for biphenyl-d_{10} in lucide.

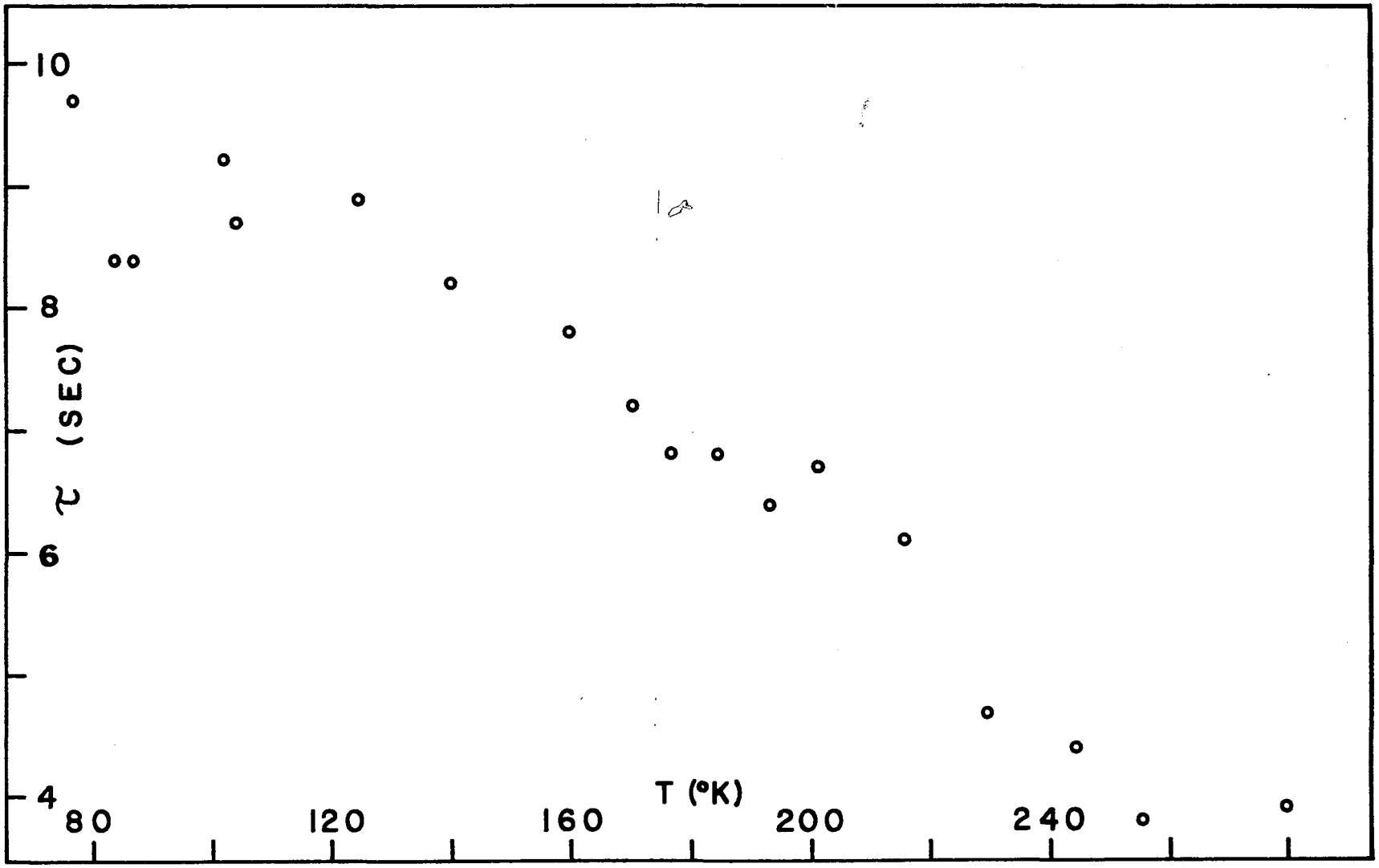

10
8
6
4
τ (SEC)
80
120
160
200
240
T (°K)

FIGURE 46. Lifetime versus temperature for phenanthrene-h_{10} in lucite.

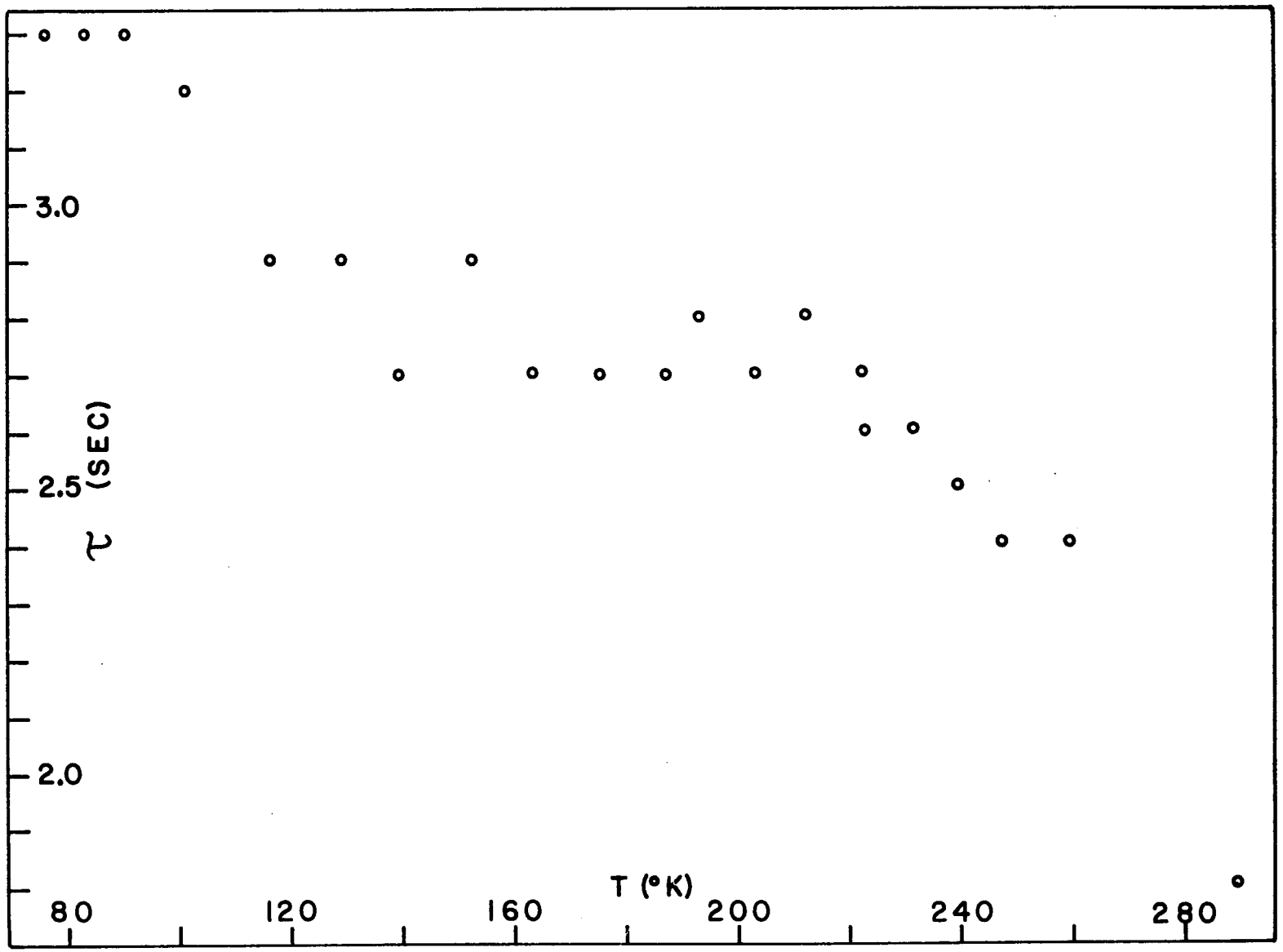

3.0
2.5
2.0
τ (SEC)
80
120
160
200
240
280
T (°K)

FIGURE 47. Lifetime versus temperature for phenanthrene-d_{10} in lucite.

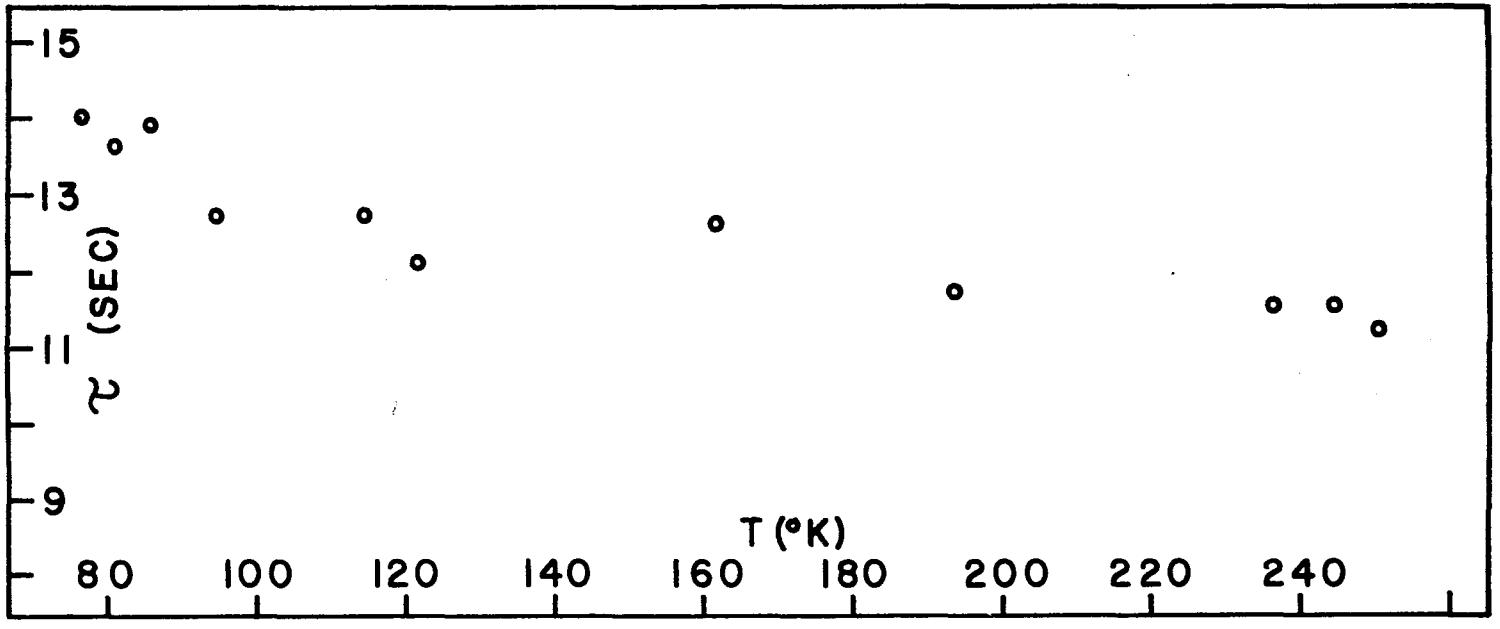

15
13
11
9
τ (SEC)
T (°K)
80
100
120
140
160
180
200
220
240

FIGURE 48. Comparison of τ/τ_o *versus* temperature for (1) biphenyl-d_{10} (filled circles), and (2) biphenyl-h_{10} (open circles), both in lucite.

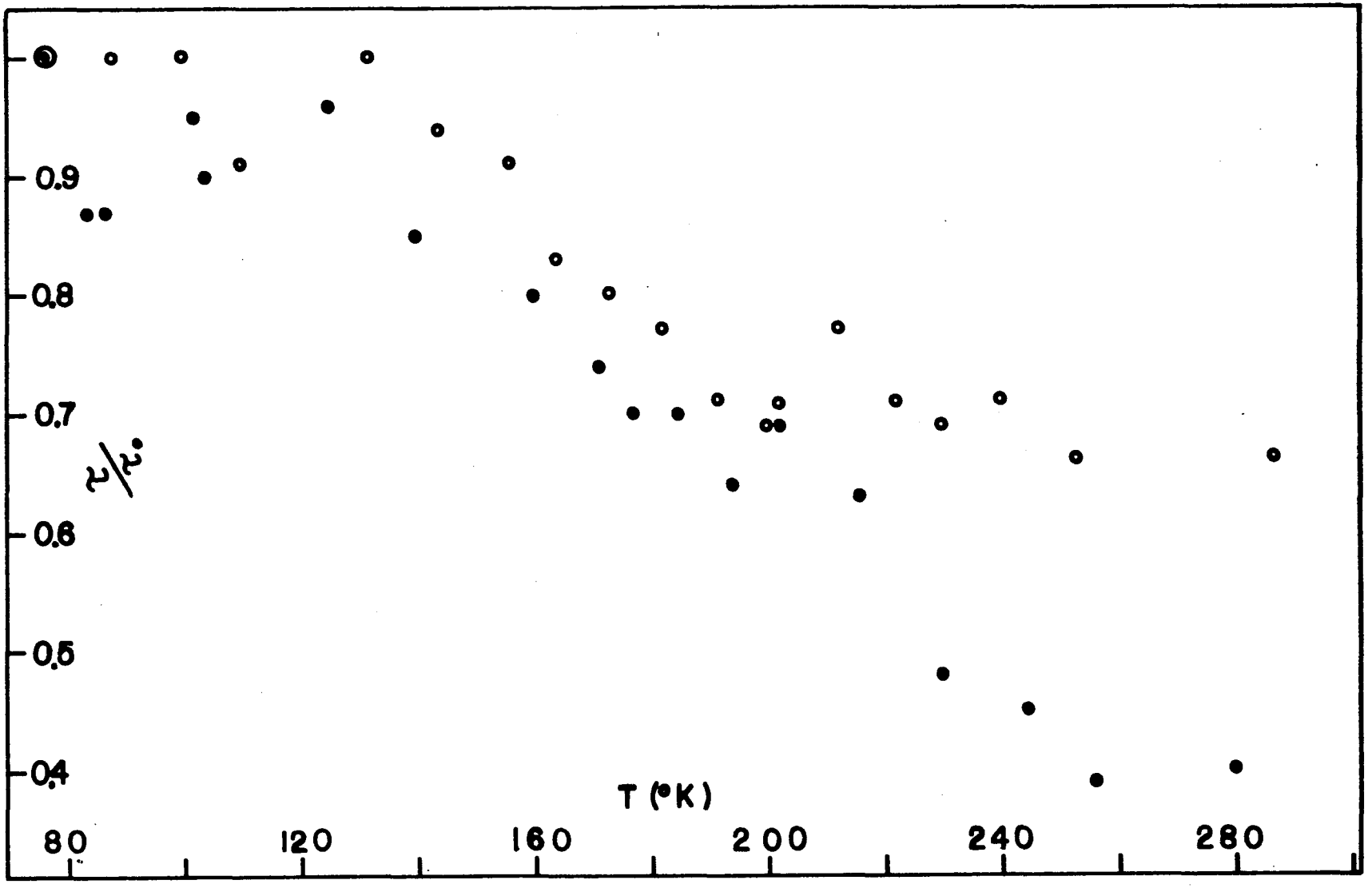
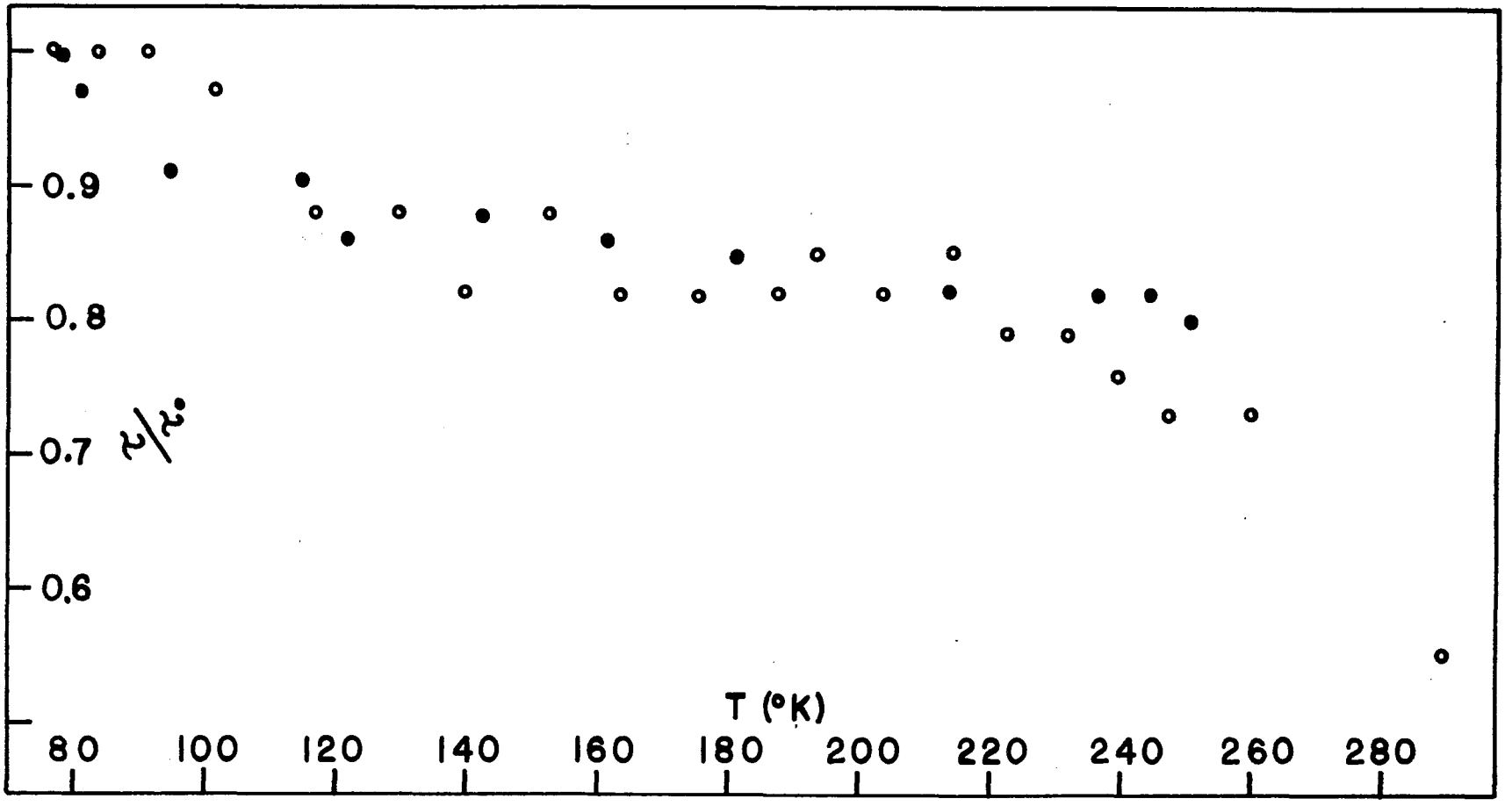

0.9
0.8
0.7
0.6
0.5
0.4
χ/χ_0
T (°K)
80
120
160
200
240
280

FIGURE 49. Comparison of τ/τ_0 *versus* temperature for (1) phenanthrene-h_{10} (open circles), and (2) phenanthrene-d_{10} (filled circles), both in lucite.


0.9
0.8
0.7
0.6
ν/ν_0
T (°K)
80
100
120
140
160
180
200
220
240
260
280

a difference in the constants for phosphorescence quenching of the protonated and deuterated samples. The equation

$$k_P = k_P^o + k_{QP}(T) + k'_{QP}\exp(-\Delta E/kT) \qquad (47)$$

is of no importance at this time, for we saw no sharp downturn in the lifetime behavior with temperature, hence, no $T_1(\text{solute}) \rightarrow T_1(\text{solvent})$ activation seems present. The second term of (47) is probably responsible for the variation of this behavior for the protonated and deuterated solutes. This is an intramolecular process but, so far, the data concerning this process has not lent itself to sensible analysis.

Concerning our work in this field, it may be stated that this part of the Dissertation contributes little by way of new knowledge concerning luminescent solutes in plastic media. It merely notes the presence of two curious and inexplicable phenomena. Our experimental results do not differ from those of Kellogg and Schwenker,[24] who also were unable to come to any conclusions concerning "dark processes", as they styled radiationless transitions.

c) Other, recent work –

Recently, Kropp and Dawson[25] studied coronene in polymethylmethacrylate and in DER-332, a Dow Chemical Company epoxy resin. They employed a method similar to the one used here to study solute luminescence in plastics; they covered the temperature range from 77° K to 400° K. Our work with phosphorescence lifetime as a function of temperature yielded the same result as did theirs within the temperature range which we covered. Our highest temperature, however, was only 290° K. Above this temperature, Kropp and Dawson report a sharp drop in the lifetime of coronene phosphorescence with temperature. Upon

making Arrhenius plots as described here in Chapter II for coronene-h_{12} in both polymethylmethacrylate and DER-332, they report finding an activation energy of 4900 cm^{-1}; for coronene-d_{12} in polymethylmethacrylate the value was 5800 cm^{-1}. They conclude that there is thermal activation of energy from the triplet state of the aromatic solute to the triplet state of the plastic matrix. Thus, it seems strongly indicated that in plastic matrices there is also an intermolecular radiationless process which is properly represented by the third term of (47). Our ideas concerning these processes had taken a similar direction; however, our experiments failed to yield any lifetime data above 290° K because the phosphorescence intensity was too low to allow measurements of its lifetime.

Kropp and Dawson state, however, that there are also some intramolecular radiationless processes yet to be clarified. These processes are greatly affected by vibrational modes[26] and by Frank-Condon factors.[27-29] Thompson[30] also makes this inference; however, a tunnelling phenomenon has also been suggested.[31]

CHAPTER IV

LUMINESCING SOLUTES IN ALCOHOLIC SOLVENTS

1. Introduction

Most studies of luminescing solutes in solvents which are liquids at room temperature are made at constant temperature. When phosphorescence is to be studied, this temperature usually is 77° K, the temperature of boiling liquid nitrogen since that temperature is easy to maintain.

It is not the usual practice to employ such solvents in temperature dependence studies such as were carried out using mixed crystals systems and plastic matrices. Von Foerster[32] studied the temperature dependence of the phosphorescence lifetime of several solutes (coronene, fluoranthene, phenanthrene, chrysene and brasan) in 2-propanol. He varied the temperature from 77° K to 110° K. The behavior of the phosphorescence lifetime of these solutes in this temperature range is shown in Figure 50. It is seen here that the lifetimes approach zero as the temperature approaches 110° K. The melting point of 2-propanol is 190° K. There is no apparent reason why the aromatic solutes should behave as the figure illustrates. We decided to extend the range of the temperature studies to see what sort of behavior the aromatic solutes exhibited. It was thought that some information might be gained about radiationless transitions.

2. Experimental

a) Apparatus

The apparatus used in these studies was identical to that used in the other studies reported here with the following modification: the

FIGURE 50. Lifetime versus temperature behavior of various aromatic solutes in 2-propanol.

70
80
90
100
110
1
2
3
4
5
6
7
8
9
τ (SEC)
1
2
3
4
5

sample was contained in a quartz tube 2 mm in diameter. The tube was fitted with a thermocouple which was immersed in the sample; the tube was also fitted with a side-arm so that evacuation and sealing would be possible.

b) Chemicals

Phenanthrene-d_{10} was the only solute used; it possesses phosphorescence of strong intensity and long lifetime. This solute was used as prepared for mixed crystal work. The solvents were spectrograde and were checked for luminescence before using; they were found to be satisfactory.

3. Results and discussion

a) Results and discussion of this work

The first trial at raising the temperature above 110° K in order to observe phosphorescence and measure its lifetime was done using a solution which had not been degassed. A phosphorescence spectrum of phenanthrene-d_{10} in 2-propanol was made at 80° K; the concentration of solute was 10^{-4} M. This spectrum is shown in Figure 51. The spectrum of the same solute in polymethylmethacrylate at 77° K is shown in Figure 52. In both cases, the spectra are practically identical.

Phosphorescence lifetime measurements were begun at 77° K; the temperature was then allowed to rise in a controlled fashion as described earlier. All measurements were made when temperature of the sample appeared to be constant (as seen on the recorder) and when the phosphorescence intensity was constant. The latter was often difficult to achieve in this system, for in certain temperature ranges the phosphorescence intensity was very sensitive to temperature changes too

FIGURE 51. Phosphorescence spectrum of phenanthrene-d_{10} in 2-propanol.

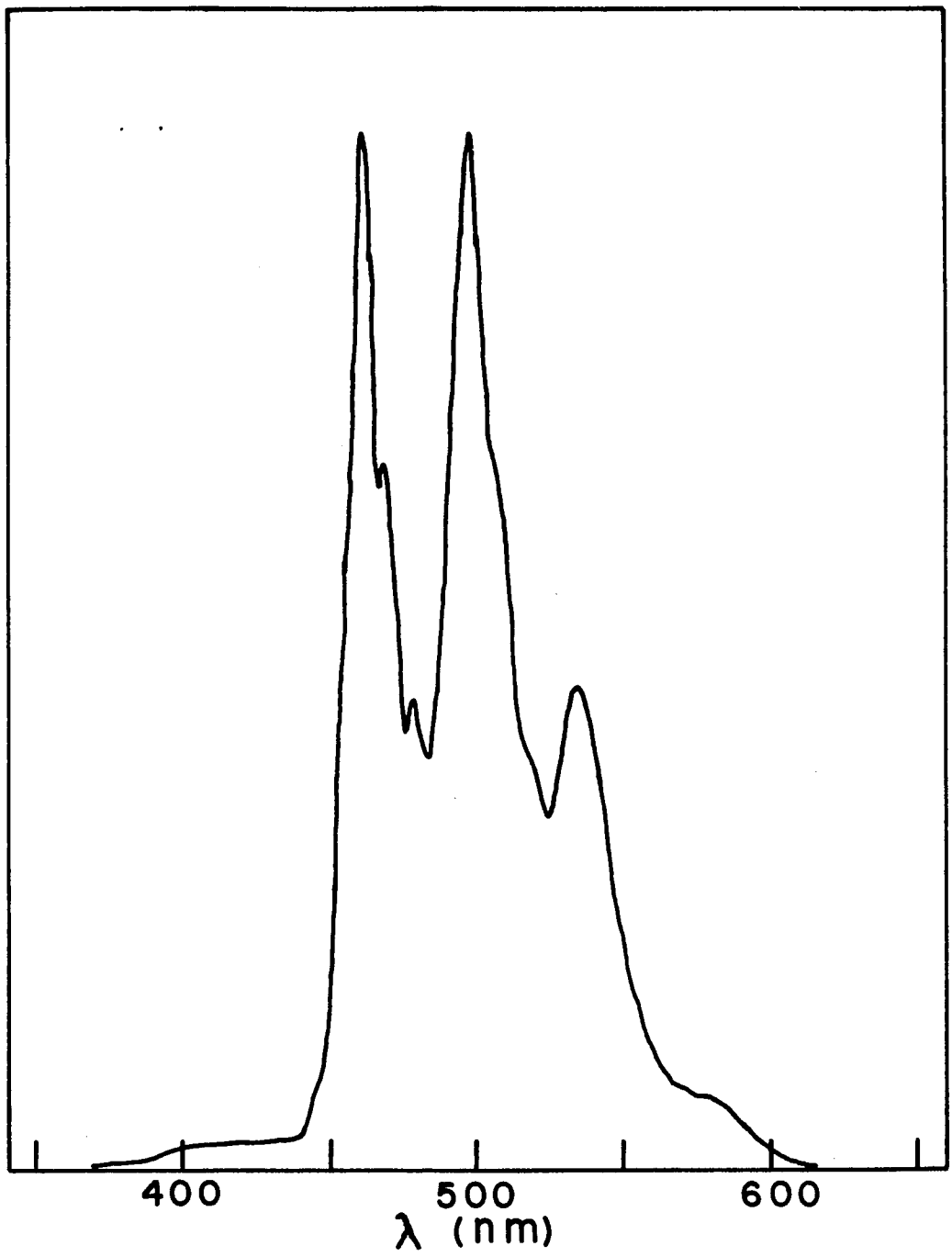
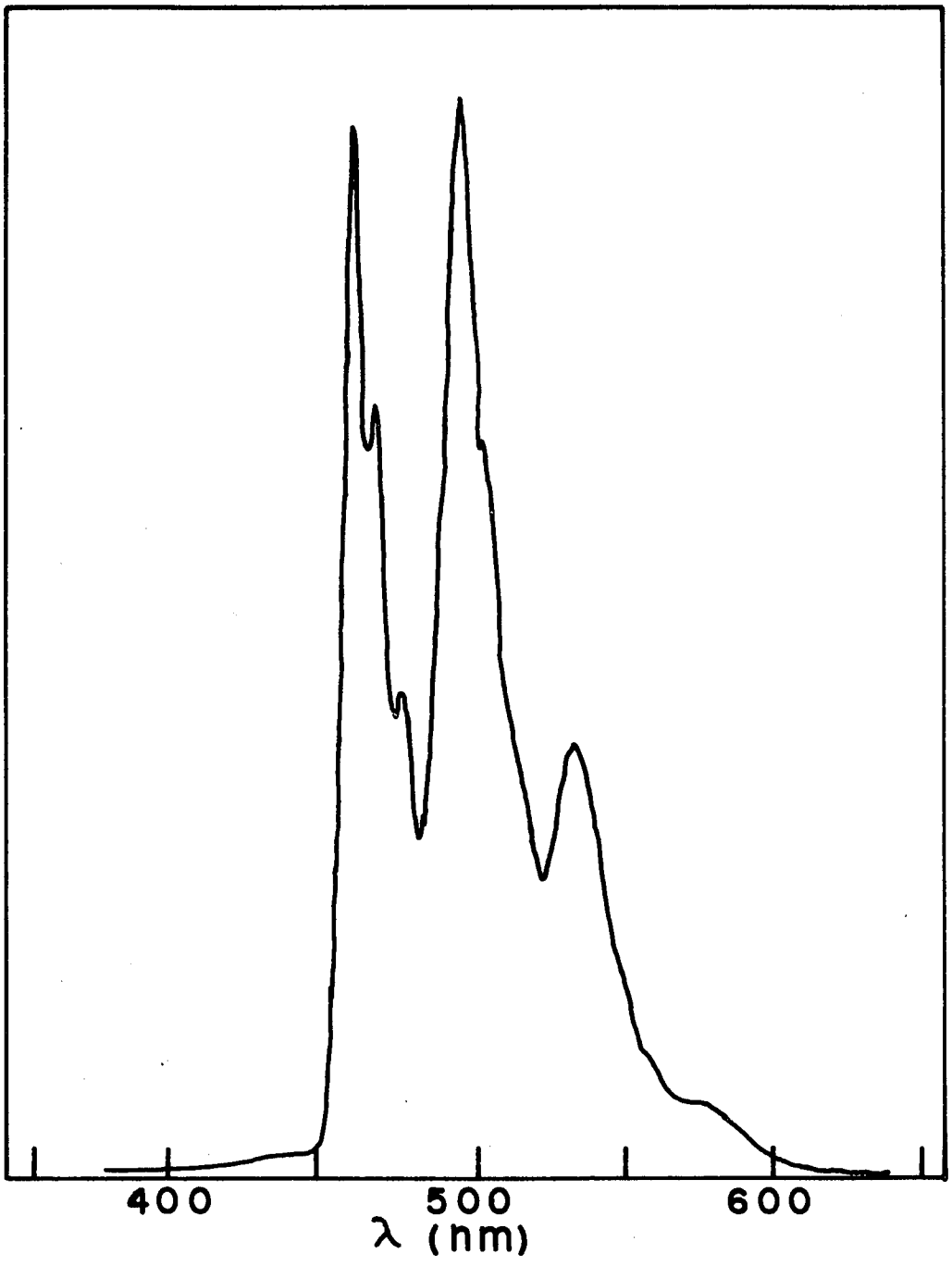

400
500
600
λ (nm)

FIGURE 52. Phosphorescence spectrum of phenanthrene-d_{10} in lucite.


400
500
600
λ (nm)

small to register on the recorder which constantly monitored the temperature. As 110° K was approached, the lifetime of the phosphorescence dropped to one-third of its original value; this is shown in Figure 53. The rate of decrease of phosphorescence intensity was very large. This intensity did not disappear altogether, but it was too low to allow measurement of the lifetime. The rate of phosphorescence decay in the region 110-128° K appeared to be of order greater than 1. The region 110-128° K gave some difficulty in controlling the temperature. At 128° K and above, the lifetime and intensity both approached their former values. Thereafter, the lifetime gradually decreased with temperature until about 165° K, where a fast downturn was noted. No decay of order greater than one was observed. At 182° K the lifetime was measured and found to be nearly 2 seconds. The behavior of the phosphorescence intensity with temperature for a non-degassed sample of phenanthrene-d_{10} in 2-propanol is shown in Figure 54.

An identical solution was next degassed by four freeze-thaw cycles and the same measurements were made as previously described. This time, however, measurements were made at decreasing temperatures and the first was made at 195° K, the temperature of the onset of phosphorescence. Examination of Figure 55 shows that at no temperature did the intensity decrease to such a value that no lifetime measurement was possible. When 77° K was reached the measurements of lifetime were made with increasing temperatures. It is seen that the behavior is essentially the same as with decreasing temperature. The minimum in the phosphorescence lifetime is reached now at a temperature between 110-117° K.

The next solution studied was degassed by nine freeze-thaw processes and lifetime measurements were made. Figure 56 compares these

FIGURE 53. Lifetime versus temperature behavior of phenanthrene-d_{10} in 2-propanol, non-degassed.

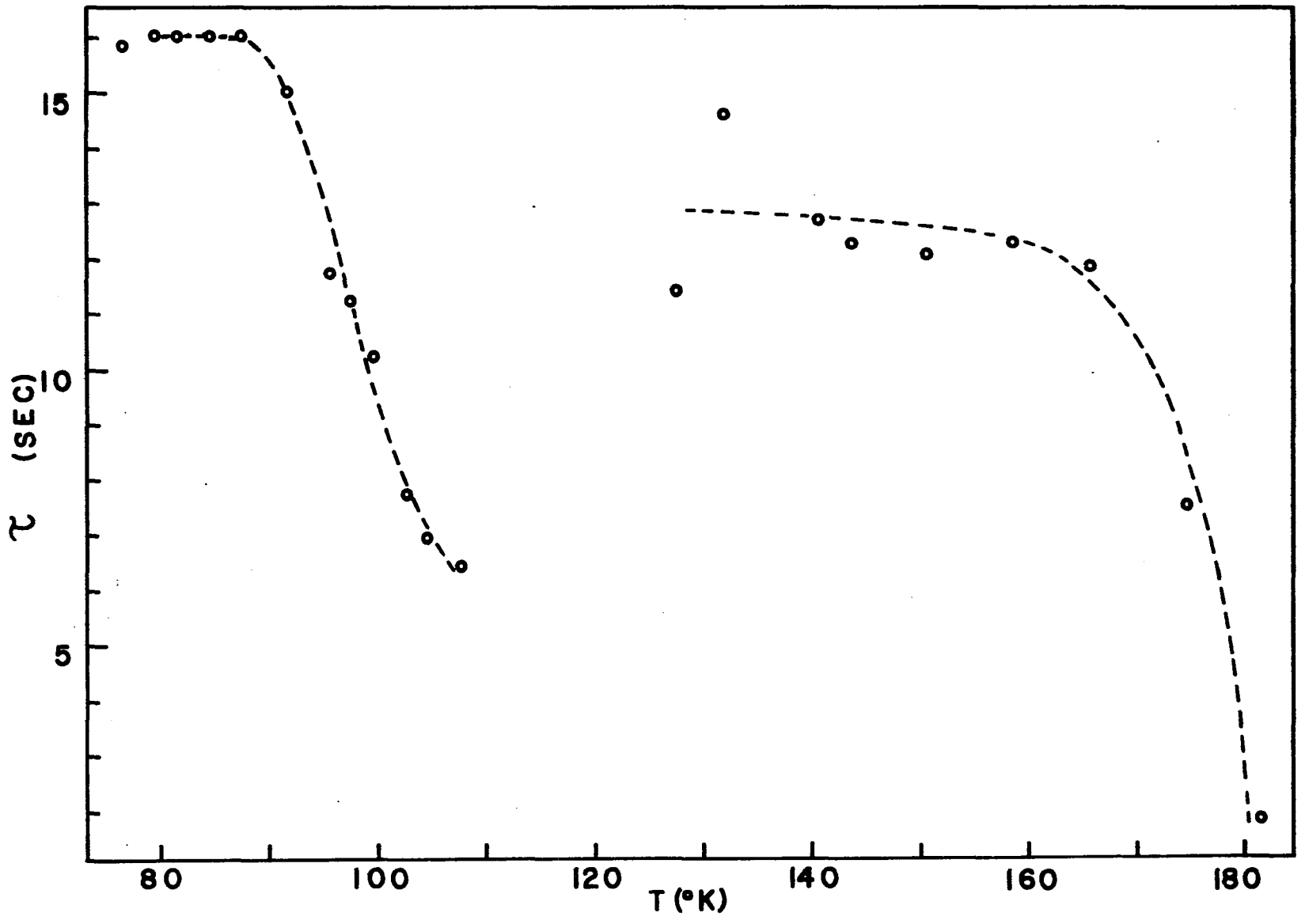

15
10
5
τ (SEC)
80
100
120
140
160
180
T (°K)

FIGURE 54. Relative intensity versus temperature behavior of phenanthrene-d_{10} in 2-propanol. Broken line -- degassed by nine freeze-thaw cycles. Solid line -- non-degassed.

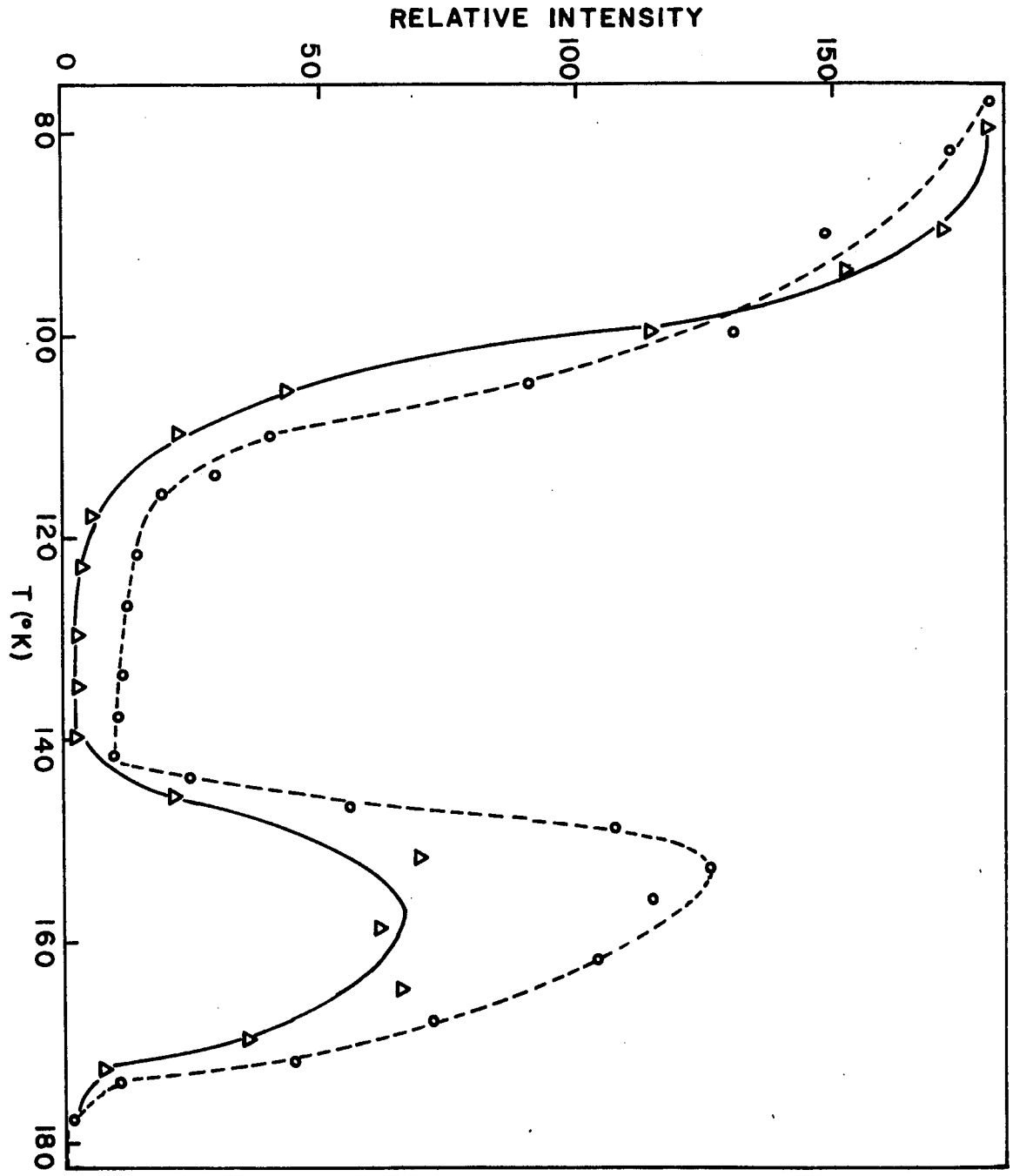

RELATIVE INTENSITY
0
50
100
150
80
100
120
140
160
180
T (°K)

FIGURE 55. Lifetime versus temperature for phenanthrene-d_{10} in 2-propanol. Open circles -- decreasing temperatures. Filled circles -- increasing temperatures.

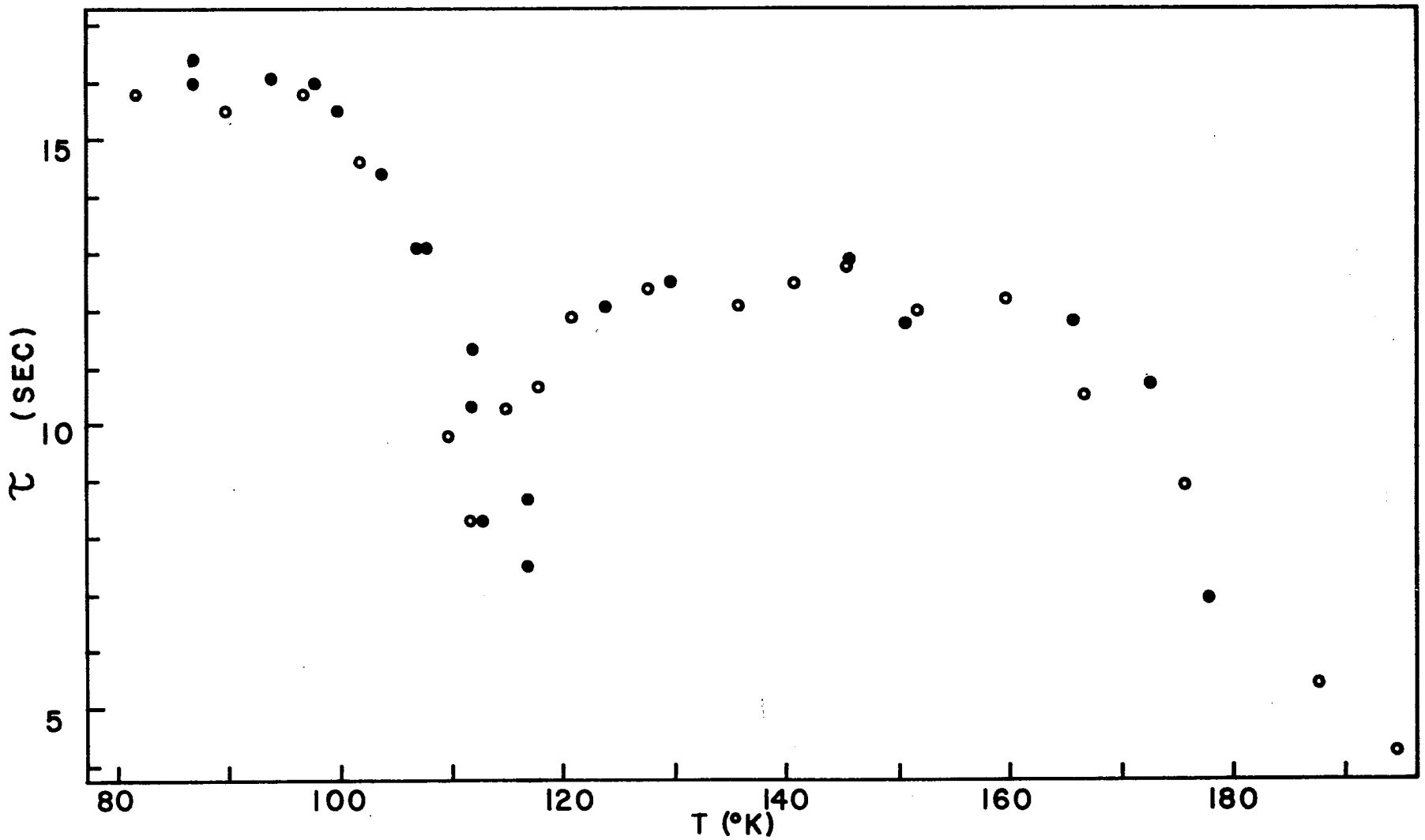
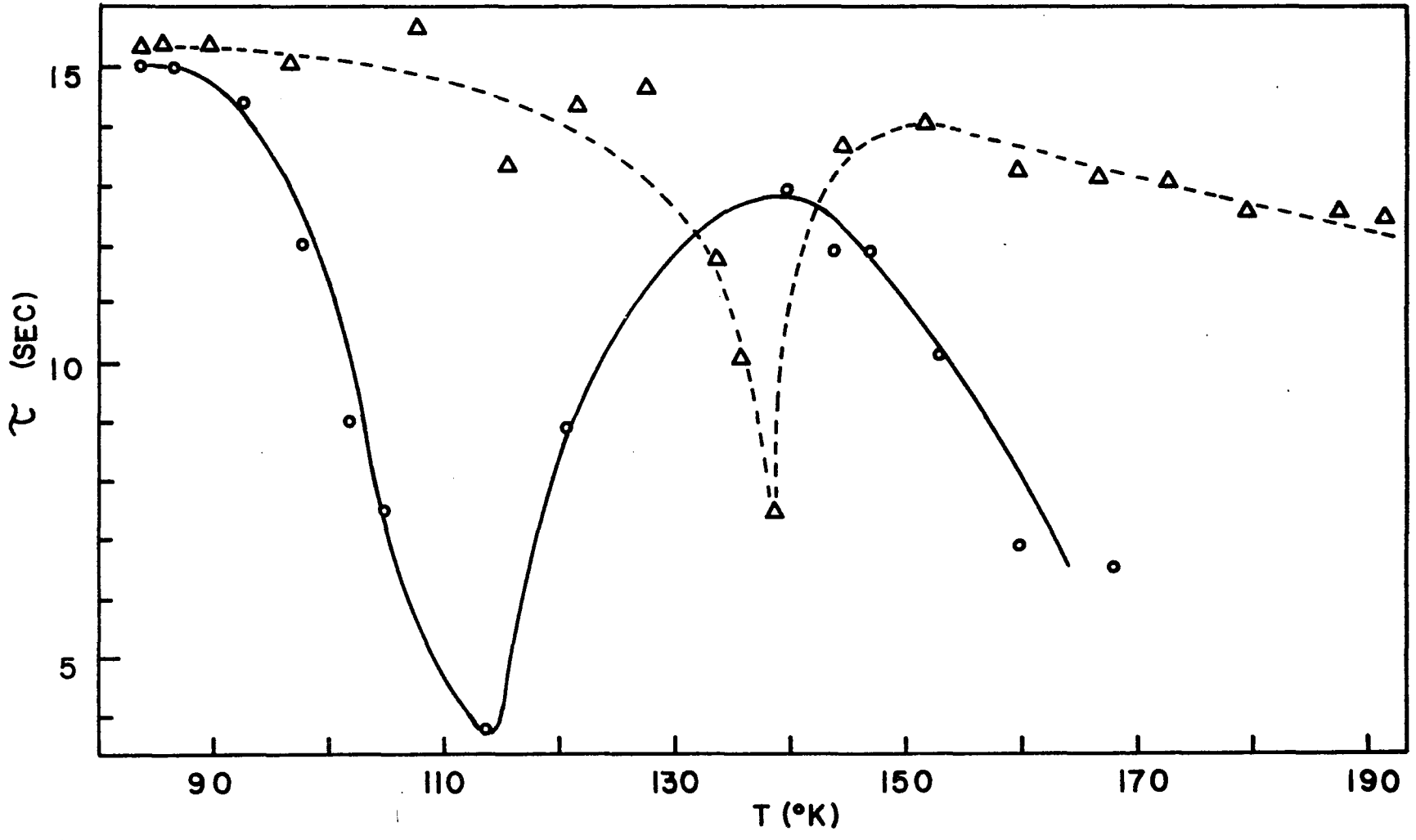

15
10
5
τ (SEC)
80
100
120
140
160
180
T (°K)

FIGURE 56. Lifetime versus temperature for phenanthrene-d_{10} in 2-propanol. Broken line -- degassed by nine freeze-thaw cycles. Solid line -- non-degassed.


15
10
5
τ (SEC)
90
110
130
150
170
190
T (°K)

measurements with a non-degassed sample. A minimum for the lifetime of phosphorescence behavior in this sample appears at slightly below 140° K. In this case, the intensity of phosphorescence decreases rapidly from 80° K and the rate of decrease is greatest at 110° K, but never reaches the lower value which the non-degassed sample reaches. In the temperature range 140-180° K the degassed sample recovers about twice the phosphorescence intensity which the non-degassed sample does. There is here, however, no qualitative difference between the two samples as exhibited by this graph. The non-degassed sample and the sample degassed by nine freeze-thaw cycles exhibit great qualitative differences in lifetime behavior as shown by Figure 56.

It was next desired to use a different alcohol in which to make phosphorescence lifetime measurements; n-butanol (m.p. 183° K) was chosen, for phenanthrene-d_{10} dissolved easily to form a 10^{-3} solution and it had a melting point only five degrees lower than did 2-propanol (m.p. 185° K). Figure 57 is the phosphorescence spectrum of phenanthrene-d_{10} in butanol. It is seen that this spectrum is practically identical to those emission spectra of the same solute in 2-propanol and in polymethylmethacrylate. Lifetime and intensity measurements for this system were made as before and plotted against temperature, the results of which are shown in Figure 58. The behavior of lifetime with temperature for the sample which was not degassed is very much like those systems of the same solute in 2-propanol. The minimum of the lifetime falls at 115° K. Between 120-140° K the phosphorescence intensity is very low and the decay of that intensity is higher than first order.

FIGURE 57. Phosphorescence spectrum of phenanthrene-d_{10} in butanol.

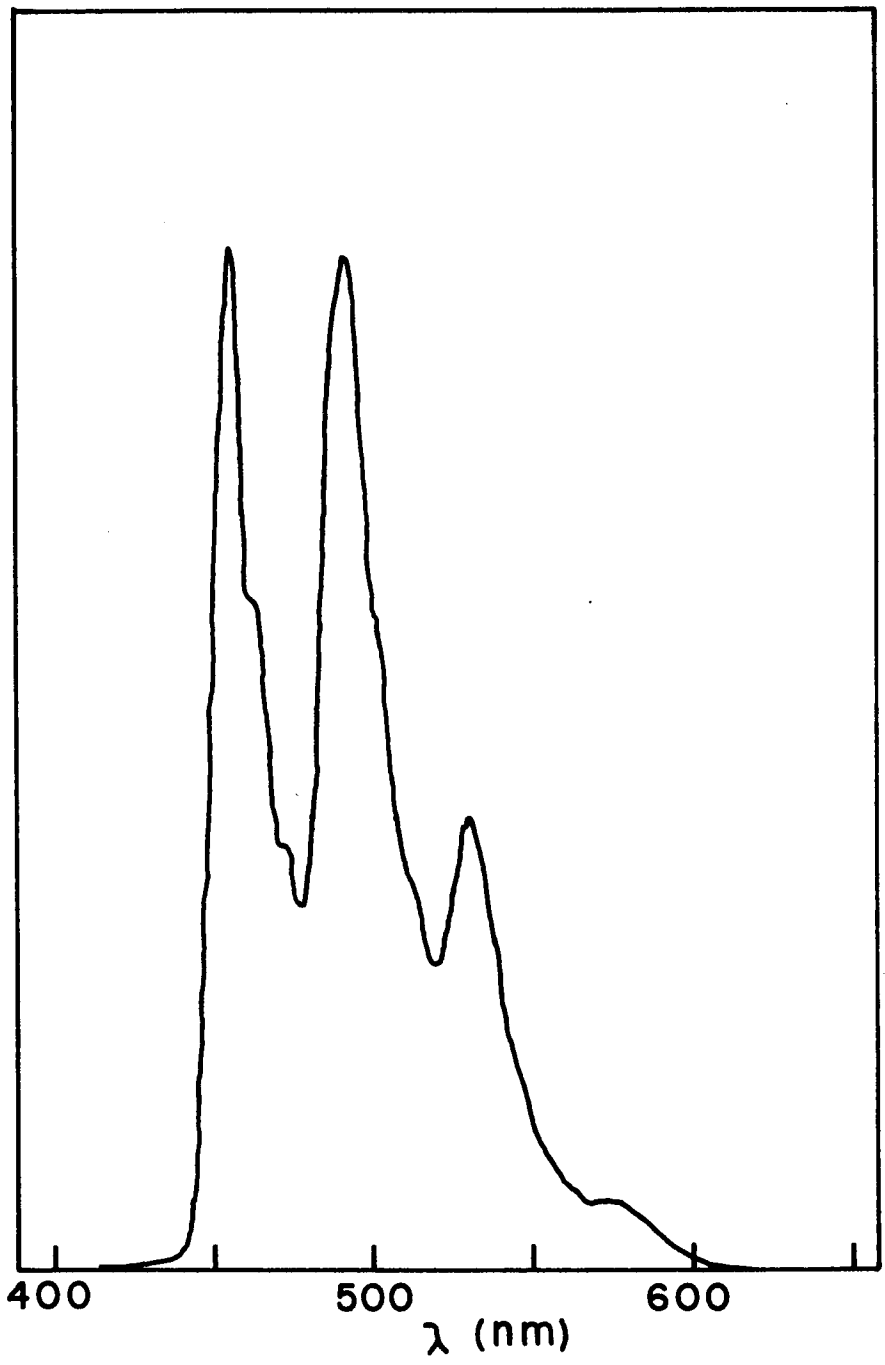
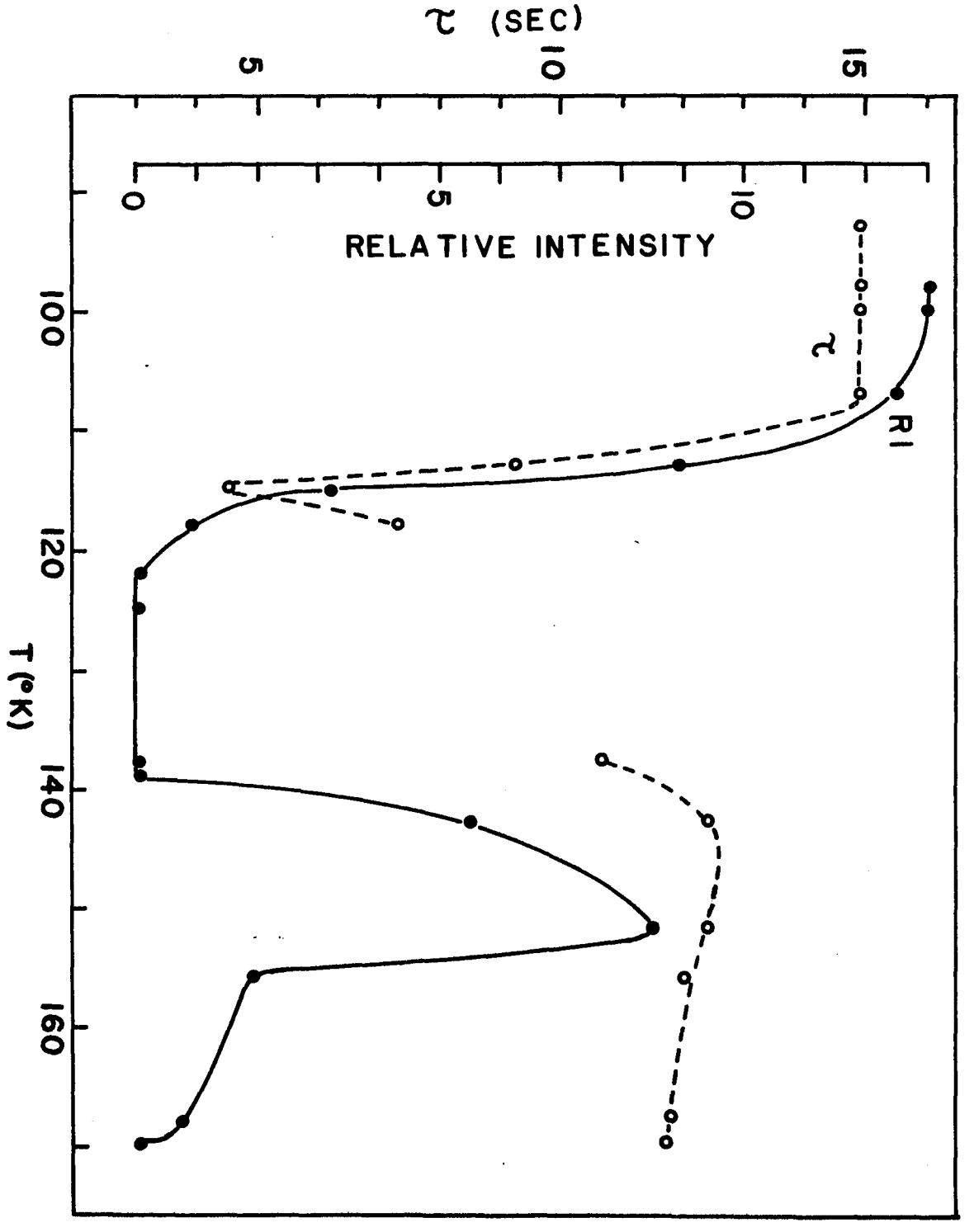

400
500
600
λ (nm)

FIGURE 58. Lifetime versus temperature and relative intensity of phosphorescence versus temperature for phenanthrene-d_{10} in butanol. Non-degassed.


τ (SEC)
5
10
15
0
5
10
RELATIVE INTENSITY
τ
RI
100
120
140
160
T (°K)

From the results of von Fœrster, in which the phosphorescence lifetimes of several different aromatic hydrocarbons in 2-propanol and in hexane were investigated, a sharp decrease in the lifetimes is evident at 110° K in the alcohol but no such behavior is seen in a hexane solvent. Hexane behaves like the plastic matrix systems and like mixed crystals where ΔE is greater than 3500 cm^{-1}. These results of studies with alcohol solvents are reported here with the additional data on the behavior of phosphorescence intensity as well as the lifetime behavior of the solute at temperatures exceeding 110° K. These results indicate that dissolved oxygen plays a large part in the behavior of the lifetime but has little effect on the intensity of phosphorescence as the temperature is varied. The dissolved oxygen can then explain only part of this behavior. No phase change is known for alcohols and if there were, it would scarcely account for the broad temperature regions in which the phosphorescence intensity is very low (120-140° K). In terms of $[T_1]$ and the rate constants, k_{QP}, it can be stated that the radiationless rate constant, k_{QP}, for phosphorescence quenching, and $[T_1]$, the triplet concentrations, are both affected up to 110° K in the non-degassed samples, since both the lifetime and intensity of phosphorescence decrease at very nearly the same rate. In the region above 140° K both lifetime and intensity recover about two-thirds of the original values, but as the melting point of both alcohols is approached (~180° K) it is seen that $[T_1]$ and k_{QP} change rapidly and not in a "compensating" fashion for the lifetime does not decrease along with the phosphorescence

intensity. Here too, oxygen has an effect on phosphorescence lifetime. For the sample which was degassed with nine freeze-thaw cycles (Figure 56), the phosphorescence lifetime was measured seven degrees above the melting point. The phosphorescence intensity was weak, but sufficient to make the measurement of lifetime. This was not possible for the non-degassed sample which exhibited some phosphorescence intensity but whose decay was not first-order.

Butanol behaved essentially the same as did the 2-propanol as a solvent for phenanthrene-d_{10}. At 170° K the butanol system which was not degassed had no phosphorescence intensity, but the lifetime had decreased to slightly under twelve seconds from a maximum of nearly fifteen seconds. This is different from the 2-propanol system which was not degassed, for the lifetime of the propanol system decreased rapidly after it reached a maximum at 140° K.

b) Summary

The results of the two systems may be summarized as follows:

1) Qualitatively there is no difference in the phosphorescence intensity-temperature graphs for the degassed and non-degassed isopropyl alcohol solution; this qualitative likeness extends to the butanol solution as well.

2) Dissolved oxygen has an effect on the lifetime of the phosphorescence by enhancement of the phosphorescence quenching process, or conversely, by increasing k_{QP}.

From 1) and 2) above, it may be restated that the two effects are completely independent of each other at lower temperature (110-140° K). Dissolved oxygen in the alcohol decreases the lifetime of the

phosphorescence as the temperature is raised, but does not greatly affect the phosphorescence intensity. To account for the latter effect, another factor is involved and this must be due to the nature of the solvent itself. There are apparently some weak interactions of the aromatic solute and the alcohol solvent which intensify as the temperature is raised to 110° K and which retains this degree of interaction until the system acquires enough vibrational energy at 140° K to destroy the interaction. The nature of the interaction itself is at this point a matter of conjecture, but it may tentatively be termed a "complex"; this term is used here with caution, however, due to the documentation of knowledge about true molecular complexes.[33] Employing this tentative and perhaps inaccurate concept concerning these processes, the suggestion might be advanced that at ~80° K the solute absorbs energy to go to some excited state, singlet or triplet; in this excited state it forms a "complex" with solvent molecules. In this complex the "normal" luminescence properties of the solute are inhibited until the temperature exceeds 140° K; this temperature allows a recovery of an increase in the phosphorescence intensity and of the lifetime. The process of "complexation"may be illustrated in the following way; A is the aromatic solute and S is the alcohol solvent:

$$A \cdot (S)x + h\nu \rightarrow A^* \cdot (S)x \rightarrow (ASx)^*$$

This interaction is presumed not to function below ~80° K nor higher than about 150° K. The species (ASx)* is the "complex" in which the aromatic solute is without the ability to luminesce. This ability to inhibit the solute emission properties (and therefore perhaps the absorption properties) is a characteristic of the two alcohol solvents,

since we have seen that 2-propanol and butanol have very similar gross effects and only differ in detail.

c) Other work with alcohol solvents

An alcohol has been used[34] in Stern-Volmer studies on luminescing solutes but these results are of doubtful value to us, for the alcohol was tertiary and no strong interactions with alcohol are seen for that system. The interaction seen here is probably the alcohol interacting with the aromatic solute; Basila et al. postulate that a small number of solvent molecules become associated with a solute molecule.[35] Work similar to theirs reported by Szepaniak and Tramer[36] shows that polynuclear aromatics exhibit very weak interactions by hydrogen bonding to alcohols. That hydrogen bonding[37] is strong enough to deactivate the luminescing solute at higher temperatures is questionable. Oxygen as an electron donor to iodine where this oxygen is a bound atom in an ether[38-41] and in a diether,[42] may somehow help clarify this problem. If such a bound oxygen atom in an ether can donate a pair of its non-bonding electrons to an empty orbital of iodine, perhaps a non-bonding pair from an oxygen atom of an alcohol also has donor properties. It may be that in the temperature range 110-140°K this bound oxygen atom donates a pair of non-bonding electrons to an anti-bonding orbital of the aromatic.

Recent work[43,44] shows that there are strong interactions between diethyl aniline and certain aromatic compounds; the complexes thus formed are not specified as to structure, but that the nitrogen atom of the amine group affects this interaction is a strong possibility.[45] That oxygen could enter into such strong interactions is still an open question.

4. Conclusions

It is clear that the behavior of the phosphorescence lifetime of the aromatic solute as a function of the temperature in alcoholic solvents is not at all understood. These studies have not resulted in a better understanding of the changes which take place in the relative magnitudes of rate constants. It would be desirable to have absorption spectra at regular intervals of temperature; this would be of aid in the interpretation of the emission spectra provided the absorption spectra would also exhibit significant changes.

This work, like that of systems of aromatic solutes in polymethymethacrylate, does not contribute anything to the understanding of radiationless processes. It does present the results of quite a lot of experimentation which raises more questions than has the work of Von Foerster, but it has answered none of the prior questions.

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